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ON THE ATTRACTIONS OF CRYSTALLINE AND ISOTROPIC MASSES AT SMALL DISTANCES.

By A. Stanley Mackenzie.

IN discussing the elastic solid theory of refraction in physical optics, it is customary to introduce an optical density which may be different in different directions. In uniaxal crystals there are two such densities, one along the optic axis, and the other in any direction in a plane perpendicular to the axis: in Iceland spar their square roots are as 1.486 to 1.658. The question naturally arises, does this property depend upon the distribution of the mass with reference to the optic axis; and, if so, could a crystal attract a particle in a manner dependent upon the position of the particle with reference to the axes of the crystal, so that it would act as if of greater mass (and therefore density) in one direction than in another?

We might give a meaning to linear density in this way. Consider, for simplicity, a uniaxal crystal such as Iceland spar. Suppose the crystalline structure is due to a symmetrical arrangement of similar particles, and that either (1) these are closer together (or farther apart) in a plane perpendicular to the optic axis than in the direction of this axis; or (2) that they are longer (or shorter) in the direction of the axis than in the plane perpendicular to it, where all their dimensions are the same. Let us cut out a spherical piece of the mass. Imagine a cork-borer whose cross-section is of the di-

mensions of that of a particle. If we bore with this along a diameter parallel to the optic axis, we shall inclose in it a different number of particles from that which we should get if we bored with it in any direction through the center of the sphere perpendicular to the axis. We might then say that the densities in these two directions were measured by the number of particles included.

In order to find out how such a crystal would attract a particle at an outside point, I have made calculations based on several conjectures as to the structure of the mass. Of these the following will serve as an example. I have supposed the sphere made up of separate equidistant layers of homogeneous matter parallel to a plane perpendicular to the optic axis: this contains both the suggestions above mentioned. In framing such an hypothesis as to the arrangement of the particles, it has to be remembered that the optic axis is only a direction in the body, and that all lines parallel to it have the same properties; also that all the layers must be of the same nature, and differ only as to size. Taking the formula for the potential of a disk, in terms of spherical harmonics at an external point, whose angular distance from the optic axis is θ, and summing for a number n of disks which will just make up the sphere, terms in $\cos\theta$ enter; these terms have coefficients of the dimensions $\frac{1}{n}$, $\frac{1}{n^2}$, etc.[1] Now n has to be taken very large (of the order of magnitude of the number of particles in a unit of length), and so these terms are negligible. Other suggestions were followed out to the same conclusion, as might be expected, that no arrangement of the constituent particles could produce a measurable difference in the magnitude of the force of attraction of such a crystal at an outside point, however its optic axis might be oriented with respect to that point — provided the law of attraction were that of Newton. Of course such proof is entirely negative, — the guesses as to formation may be far from the truth, and Newton's law may require modification, — and so it was thought that it might be well to try experiment. When two spherical masses, at a distance apart comparable with their radii, attract each other, we know from the experiments of Cavendish,[2] Reich,[3] Baily,[4] and

[1] See Appendix.
[2] Phil. Trans. 1798.
[3] Freiberg, 1838, and C.R. 1837.
[4] Phil. Mag. 1842.

Cornu and Baille,[1] that the attraction obeys the Newtonian law within the limits of the agreement of their results, and that "distance between them" means the distance between their centers, which also admits of mathematical proof; but it should be remembered that because this law is true for heavenly bodies it does not follow that it should hold good for the case investigated by Cavendish. It is of interest to find that it is upheld as this experiment is performed with apparatus of smaller and smaller dimensions. Professor Boys' investigation, promised in his paper in the *Proceedings Royal Society*, Vol. 46, ought to be of special interest.[2] At the end of this paper will be given the results of a series of experiments made to test this law directly. They are necessarily rough, as the apparatus was designed for qualitative measurements. In the case of crystals, it is still less allowable to assume that Newton's law is obeyed, and to say that a spherical mass of crystalline matter will give the potential at an external point the same as if it were an equal mass concentrated at its center of figure. It was thought worth while to test the case experimentally, and the following experiments undertaken at the suggestion of Professor Rowland were begun with that end in view. The form of the apparatus described is similar to that employed by Professor Boys in his paper referred to. In the following pages will be given a description of the apparatus and methods employed, and the results found. It will be seen that there is no deviation from the law of Newton, within the limits of observation, either in the case of attracting crystalline matter with reference to its optic axis, or in the case of isotropic matter at small distances.

Description of Apparatus.

The suspended system consisted of a light beam *AB* (Figs. 1 and 2) joined to the hook of the suspending fiber by a rod *CD*, which also carried the mirror *m*; a brace *ACB*, being a continuation of the beam, was used to give sufficient rigidity. The whole was made of very fine aluminium wire. The mirror was of plain

[1] C. R., Vols. 70, 76, and 86.

[2] Since this was written Professor Boys has published a paper on this subject. See "Nature," Aug. 2, 1894.

glass silvered on the back, and was 1 cm. in diameter. At the points *A* and *B* the small masses *a* and *b* were suspended at unequal distances below the beam by means of silk fibers. This system was inclosed in a rectangular brass box (Fig. 3) whose internal dimensions are: height 11.7 cm., width 3.1 cm., and depth 1.55 cm. This box stood upon a heavy base with tripod and screws for leveling purposes, and above carried a projection upon which fitted, with carefully made cone bearings, a brass cap carrying the glass tube containing the suspending fiber. This fiber was of quartz, about 0.0003 inches in diameter. By means of the cone bearings the whole suspension could be rotated very easily, and the small masses set symmetrically within the box. The large attracting spheres were supported upon the same base that carried the box. Two pillars, *g* and *h*, screwed on to the base, carried a rectangle *cdfe*, pivoted at the middle of its two sides, *df* and *ce*, upon the pillars; upon the other two sides, *cd* and *ef*, were put the large masses, *M* and *M'*. Thus, by simply rotating the rectangle, the balls could be made to take up their position of maximum attraction, or a neutral position; they were so placed on one side and the other of the middle of the wires *ef* and *cd* that when in their positions for maximum attraction they were exactly opposite the corresponding small masses; and, accordingly, they were always rotated in one direction only from their neutral position.

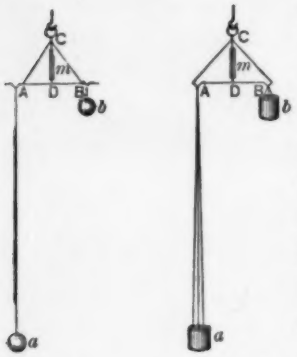


Fig. 1.

Fig. 2.

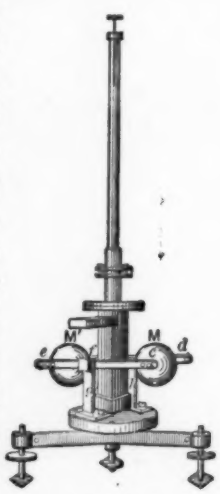
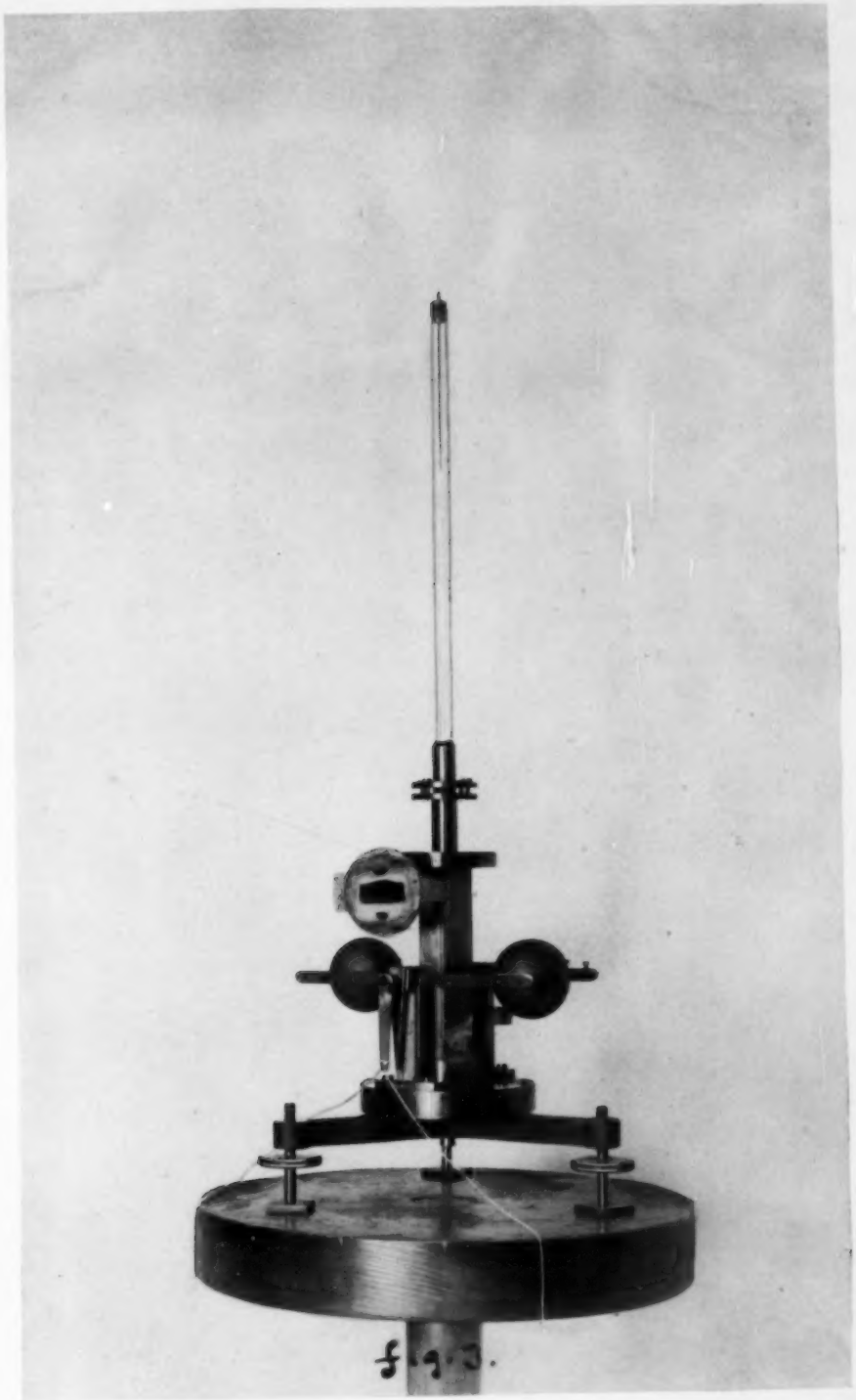


Fig. 3.

At the upper part of the box, opposite the mirror, was a hole about which fitted a funnel-shaped projection of rectangular cross-section, the end of which was covered with plane parallel glass. Through this passed the beam of light to



A. STANLEY MACKENZIE: ATTRACTION BETWEEN MASSES.

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the mirror. The motion of the suspended system was observed by means of a telescope and straight scale.

As a large deflection was sought in order to show any differences that might exist, the fiber was made as small as possible and the period large. Twice during the experiments the fiber broke in the middle, and all the previous results had to be discarded and a fresh start made. In each case the fiber had been up and under strain for weeks, had received no jar, and broke in the night when not in use, and not while it was in motion. This may have been due to bad fibers, although all fibers were carefully examined before use under the microscope in order to detect unevennesses. It was more likely due to the fact that the fiber was too heavily loaded. On account of the rapid dying out of the swings, due to the peculiar form of suspension, the period was never accurately found; but the mirror soon took up its position of rest, and that only was observed.

The box was made air-tight with "universal wax," and to still further protect the apparatus from the effects of air-currents, the whole instrument was covered by another case with a glass window opposite the window in the box. In the later experiment still further precautions were taken in order to get rid of the effects of temperature, and they will be described at a later period.

The instrument was set up in a room at about 10 feet below the surface of the ground, on a heavy table whose feet stood in boxes of coarse sawdust. In this way the surface earth tremors and the effects of sudden changes in outside temperature were entirely gotten rid of. A set of readings of the temperature of the room was taken in order to see how much it varied, due to the presence of the observer and the burning gas-jet. It was found to rise from $\frac{1}{2}$ to $\frac{3}{4}$ of a degree in two or three hours. The extremes of temperature during the whole period covered in the experiments were 14° and 21° C., and no variation of the deflections was observed due to this cause.

FIRST SERIES OF EXPERIMENTS.

Attraction of large masses of calc-spar for small lead masses.

In this series of measurements the small balls *a* and *b* (Fig. 1) were of lead, and weighed each 0.5310 grams; and the total weight suspended was 1.1653 grams. In the early part of the experiments it was observed that there were variations in the zero-point due to the presence of iron in the lead. The balls finally used were made of electrolytically deposited lead, and showed no such effects. The vertical distance between the balls was 8.80 cm., and the horizontal distance 1.50 cm.

The attracting masses *M* and *M'* were two pieces of optically perfect calc-spar cut into the form of spheres. The cutting was a difficult operation, and was done by Mr. Bohrer, lapidary, of Philadelphia. They were of different sizes, due to the grinding away of a flaw that developed in one, and had radii of 2.65 and 2.32 cm., and weighed 212.860 and 142.143 grams respectively. The supports *ef* and *cd* of the balls were pointed rods fitting into small conical holes drilled in the spar at opposite ends of a diameter. The balls could thus be turned about this diameter into any required position. A set of readings was made thus: the balls were placed horizontally in their neutral position, and the reading of the zero-point of the scale taken. They were then placed in their position of maximum attraction, and after three or four semi-vibrations the mirror was at rest, and the reading of the scale again taken. These readings were repeated several times, and the mean of the deflections taken. The crystals were then rotated into another position, and the operation of taking a set of readings repeated. The actual taking of a set of readings was very laborious and required a great deal of time, for it was generally found that the zero kept shifting more or less erratically for the first hour or two during which observations were made; it was found that this was the case even under the most favorable circumstances, and the explanation does not seem very patent. It was some time before this fact was noted, and the readings given are those taken after the zero became nearly constant. Accordingly, observations were generally continued for three or five

hours at a time, depending upon the time taken by the zero-point to become constant. The best readings were taken after ten o'clock at night, when everything was quiet and still, and trains had ceased running in the neighborhood. During one sitting readings were taking for eight continuous hours with almost exactly agreeing results during the last five. As a rule, the zero-point was never absolutely constant, but had a slowly shifting motion. This was much more apparent for the first week or so after setting up the suspended system; but by taking the average of a series of deflections no appreciable error was caused by it. Various methods of attaching the quartz fibers were tried in order to see if that would obviate this shifting of the zero-point, but loaded so near to the breaking-point as mine were, no method I tried turned out to be entirely effectual. Fibers drawn on a revolving wheel were tried, but not found so trustworthy as those made by myself after the original plan of Professor Boys by means of a bow and arrow.

The direction of the optic axis was found by means of the polariscope. The ends of the diameter parallel to this direction were marked *A* and *B* (Fig. 4). The axis upon which the crystal was rotated, was through *O* perpendicular to the section in this figure, being the line of intersection of the gliding plane through the center and the equatorial plane of *AB*. *AB* is the direction of the optic axis, and six other points are marked on the ball at 45° apart. In the following table of readings "*A* and *A*" means that when the attracting masses are rotated into their position for giving maximum deflection, the point on each ball marked *A* is nearest the corresponding small ball. The numbers given are the deflections on the scale in centimeters found as described above. The numbers in a column between two horizontal lines were taken at the same sitting.

Fig. 4.

A and A.	B and B.	C and C.	D and D.	E and E.	F and F.	G and G.	H and H.
6.1	6.0	6.0	5.9	5.9	5.8	5.9	5.8
5.9	6.1	6.1	5.95	6.1	6.2	6.1	6.1
6.1	6.1	6.1	5.95	5.9	6.0	6.0	5.9
5.9	6.0	6.0	6.0	5.9	5.9	6.2	6.1
5.9	6.0	6.0	5.9	5.95	6.1	5.8	6.0
6.1	6.0	6.0	6.0	6.15	5.9	6.0	6.0
6.0	5.9		6.05	6.0	6.0	6.1	6.0
6.0	5.9		5.95	5.9	5.9		6.1
60.	5.9		5.9	6.0			6.1
6.05	6.0		6.0	5.95			6.0
6.05	5.95		6.1				6.0
6.1	6.05		6.0				6.0
6.0			6.0				6.1
6.1			6.0				6.0
6.0			6.0				6.0
5.9			5.9				6.0
			6.1				
			6.05				
			6.05				
			6.1				
Mean 6.01	5.99	6.03	5.995	5.975	5.957	6.03	6.01

Some other positions of the balls were then tried with similar results.

A and B.	A and C.	C and D.	E and F.	G and H.
6.15	5.9	6.1	6.0	5.9
5.95	6.0	6.0	6.2	6.1
5.9	5.9	6.0	5.8	5.9
5.9	6.0	5.9	6.0	
6.0	6.0	6.1	6.0	
	6.1	5.9	6.1	
	5.95		5.9	
	6.05		6.0	
Mean 5.98	5.99	6.00	6.00	5.97

These results agree with the others, and also show that there is nothing of the nature of polarity exhibited by crystals in their attractions.

The axis of rotation was then changed to AB: Fig. 5 is a section through the center of the crystal perpendicular to this diameter: KL (Fig. 5) was the axis in the previous measurements, and C and D are the same points as before.

Fig. 5.

K and K.	L and L.	C and C.	D and D.	C and D.	N and R.
5.9	5.85	6.2	6.2	6.0	6.0
6.1	6.05	6.0	5.9	6.0	6.1
6.0	5.85	5.9	6.1	5.9	6.1
6.2	6.05	6.1	5.9	5.9	6.1
6.0	5.9	6.0		6.1	5.9
6.0	6.0	5.9		5.9	6.0
5.9	6.1	6.0		6.0	5.8
6.1	6.1	5.9		5.9	6.1
6.0	6.1	6.1		6.0	5.9
	6.1	6.0			6.0
	5.9	6.0			5.9
	5.9	5.9			6.1
	6.0	6.1			6.0
	6.1	6.0			5.9
	6.1				6.1
	6.0				5.95
	6.1				6.15
	5.9				5.9
					6.0
Mean 6.02	5.995	5.99	6.025	5.97	6.00

It will be seen from these numbers that there is no difference between these deflections. The scale was only read to $\frac{1}{2}$ mm., and these results vary among themselves by less than that amount. The average of all the mean readings given is 6 cm., and the greatest divergence of the means from it is 0.03 cm., or $\frac{1}{200}$ of the whole deflection, and most of the results are much closer, especially where many readings of the same quantity are taken. To within this amount then we find no variation of the force of attraction of a crystal at a point at a given distance from the center of the

crystal, as this point is taken in different directions with respect to the optic axis.

It might be noted that in the columns marked "*K* and *K* and "*L* and *L*" the line joining the crystal and small ball lies in a cleavage plane of the crystal, and that the attraction in this position is the same as in every other.

The conclusion must be drawn, therefore, that in so far as these measurements go, a crystal acts exactly like an isotropic body in its gravitational properties; that is, a spherical mass of it obeys Newton's law, and acts as the same mass concentrated at its center.

A series of measurements with opaque crystal balls had been made the previous year and gave similar results, but the total deflection was only 3 cm., and it was thought advisable to increase the deflection and at the same time use transparent crystals.

SECOND SERIES OF EXPERIMENTS.

Attraction of large masses of calc-spar for small masses of the same material.

In order to make the investigation more complete, it was thought interesting to substitute for the small lead balls two small masses of calc-spar, and so get the attraction of one crystal for another. If any difference did exist, this method would double the variation in the deflection: at the same time the total deflection was increased by lengthening the beam of the balance.

In this series of experiments the whole suspended system (Fig. 2) was new. The small masses were cylinders of calc-spar with the optic axis the axis of figure, and vertical. This shape was chosen on account of the difficulty of cutting such small masses into perfect spheres. The dimensions of the cylinders were 6 mm. in length and 6.99 mm. in diameter, and weighed 0.6096 and 0.6066 grams respectively.

The fiber was of quartz 0.0003 inches in diameter and 10⅓ inches long. The weight of beam and mirror was 0.1248 grams, and the total weight supported by the fiber 1.35 grams. The cylinders were suspended by three cocoon fibers each, so as to reduce the rotation, and their centers were 2.25 cm. distant horizontally, and

8.70 cm. vertically. The attracting masses were the same as before, but shifted 0.375 cm. to the right and left respectively, so as to be opposite the small cylinders. Sets of readings were taken in the same way as before described. The particular arrangement of masses and suspending fibers gave the beam an aperiodic motion, which was unexpected. The time required for the beam to come to rest was about 15 minutes. The distance from the mirror to the scale was 340.8 cm.

The following are the readings taken: not so many positions of the large masses were examined as in the earlier series, but only a few typical ones, and more readings of each taken in order to eliminate the errors of observation. In the first four columns the axis of rotation of the crystal was *KL* (Fig. 5); in the fifth column it was *AB* (Fig. 4).

A and A.	C and C.	F and F.	C and D.	C and C.
8.9	8.9	8.75	9.05	9.0
8.9	8.9	9.0	9.0	9.0
8.9	8.9	8.75	8.95	8.9
8.7	9.1	9.05	9.1	9.1
9.0	8.9	9.05	9.0	9.0
8.8	8.9	8.75	8.9	9.0
9.1	9.0	9.15	8.95	9.0
8.9	9.1	9.0	9.05	8.9
8.9	8.9	9.0		8.9
9.0	8.9	9.1		9.1
9.0	8.9	8.8		9.0
8.9	9.1	9.0		9.1
9.1	8.9	8.8		
9.0	9.0	9.0		
9.0	9.0	9.0		
9.0	8.9			
9.1	8.8			
8.75	8.9			
8.8	8.9			
8.9	9.1			
9.0	8.8			
9.0	8.9			
9.1	9.1			
8.9	9.0			
9.0	9.0			

A and A.	C and C.	F and F.	C and D.	C and C.
9.0	9.1			
8.8	9.0			
8.9	9.0			
9.0	9.0			
9.0	8.8			
9.0	9.0			
8.85	8.8			
9.0	8.9			
8.9	9.1			
9.05	9.0			
9.0	8.9			
8.9	9.1			
8.95	8.9			
8.9	8.9			
9.0	9.1			
9.0	8.9			
9.05	9.1			
9.0	8.8			
9.0	9.0			
	9.0			
	9.0			
	8.9			
	9.1			
	8.8			
	8.9			
	8.95			
	8.95			
	8.95			
	8.95			
	8.95			
	8.95			
Mean 8.95	8.96	8.95	9.00	9.00

From this second series of experiments the same conclusion must be drawn as before from the first series; that there is no difference in the deflections, and hence none in the attractions, when the crystal sphere is turned in any way about its center, which remains fixed. The total error in observation is the same as before, but the total deflection is larger, and the means closer together. Where a large number of observations was made, the means differ only by 1 part in 900; and even in those cases where

only a few readings were taken, the greatest difference in the means is 1 in 200.

Third Series of Experiments.

Verification of the law of masses.

As a further proof that these crystal spheres attract according to the law of Newton, with a force proportional to the product of the attracting masses, the large spheres of calc-spar were taken off and replaced by accurately turned spheres of lead of diameter 5.42 cm. each, and weighing 927.767 and 928.047 grams respectively. They were held by light steel wires, *cd* and *ef* (Fig. 3), passing through their centers. They were placed so that when in the position for maximum attraction, and when the little masses had come to their new position of rest, the distances apart of the centers of the attracting masses should be the same as that in the last series of experiments. By calculation and measurement this distance was 3.591 cm. in this series and 3.590 cm. in the last; that is, they were the same within the limit of error in the measurements.

The irregular motion of the beam was more pronounced in these readings than in the smaller deflections of the two preceding series, as will be seen from the readings which follow: —

46.6	46.6	46.8
47.0	46.4	46.8
46.6	47.0	46.4
46.7	46.7	46.9
46.6	46.7	46.6
		46.7
		46.8
		46.6

Mean of all 46.7.

In order to compare this deflection 46.7 with that in the case of the crystals 8.95, at the same distance, we must pass from the

scale readings to the actual angles of twist of the fiber. Calling α and α' the angles of torsion, we have

$$\tan 2\alpha = \frac{8.95}{340.8}, \text{ and } 2\alpha = 1^\circ\ 30'\ 15''.6;$$

$$\tan 2\alpha' = \frac{46.7}{340.8}, \text{ and } 2\alpha' = 7^\circ\ 48'\ 10''.$$

Therefore $$\frac{\alpha}{\alpha} = 5.187.$$

If we calculate the ratio of the forces of attraction in the two cases from the law of Newton, making corrections for the fact that the little masses are drawn from their zero positions, and that the big balls exercise a slight attraction on the small masses which are farther off as well as upon those that are near, we find these attractions should be as 5.214 : 1 ; or, in other words, the reading 46.7 should have been 47.0, in order that the experimental and theoretical numbers might coincide. The variation from Newton's law is only, therefore, about one-half of one per cent. This agreement is satisfactorily close under the circumstances, but the method is capable of better results, for, as will be seen in the next series of experiments, the instrument was not yet sufficiently guarded against slight draughts or changes of temperature, and their effects became more noticeable, the larger the deflection.

FOURTH SERIES OF EXPERIMENTS.

Direct experimental test of Newton's law of the distance.

It was thought that with the apparatus described it would be interesting to test the law of the inverse square of the distance, when the distance between the centers of the attracting bodies was small. In the Cavendish experiment, the distance was about 93 cm. ; in Cornu's, about one-quarter of this ; in Reich's, 16.8 to 19 cm. ; and in the present investigation, 3.7 to 7.4 cm. The apparatus described was not at all designed for quantitative measurements, and accordingly was not well suited for this series of experiments ; but after some preliminary observations of what I could do with it, I thought I would go on and take a series of

readings, and at the expense of time and care I was able to get much better results than might have been expected. The chief difficulty to be overcome was, of course, the measurement of the distances. The placing of the outer or larger balls symmetrically with respect to the instrument was only a matter of care in the manufacture of the instrument, and was done satisfactorily; the greatest difficulty was met in trying to place the inner beam with its suspended small masses midway between the larger masses. This difficulty arose from the fact that the inside masses could not be seen through the observing window, and so their positions could not be directly observed. A diagram will make the matter clearer. Let the figure (Fig. 6) represent the projection of the essential parts of the apparatus on a horizontal plane: *cd* and *ef* are the wires carrying the attracting masses.

The distance MM' or df can be accurately measured by the dividing engine. Also by means of the cathetometer the inner mass b can be set as much above the horizontal plane containing M and M' in their positions of zero attraction as a is below it. The remaining essential point is to have O, the middle point of the beam, exactly midway between M and M', and the beam itself parallel to cd or ef. The method adopted was the following, which proved successful although tedious. Before closing the case, the beam was set as near its correct position as was possible; then the case was closed, and the covers placed over it, and a series of deflections observed to the right and left, with the large balls in the positions M and M' (Fig. 6). If the deflection on one side differed from that on the other, the position of the beam was slightly changed in the way suggested by the results, and its correct position thus determined by trial and error.

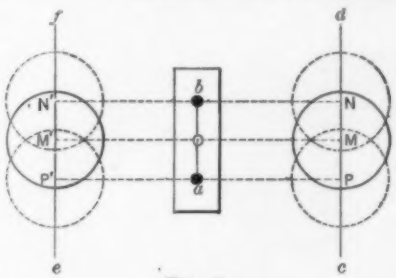

Fig. 6.

Some further precautions in addition to those already described were taken in order to overcome the slight variations of the motion of the beam that have always existed. Fitting over the

whole instrument, already made air-tight, was a copper box, and over all a great pasteboard box lined with cotton wool. Each of these coverings was made practically draught-tight where it touched the table. The large balls were moved by strings passing through these covers. It was also found effective to have a paper bottom to the table upon which the instrument stood, in order to ward off the radiations from the floor.

The frame supporting the large balls played between stops which allowed the balls to be in the position of zero attraction, or to be exactly opposite the inner balls in the position for maximum attraction. As an extra precaution, the frame carried a pointer moving over a graduated circle which could be observed from the outside through the glass windows. The setting of the beam exactly was of so much importance that these trial measurements were made with the large balls at M and M', at N and N', and at P and P'. From two to three weeks' constant work was required before this central and symmetrical position for the beam was exactly found and the apparatus ready for measurements to be made.

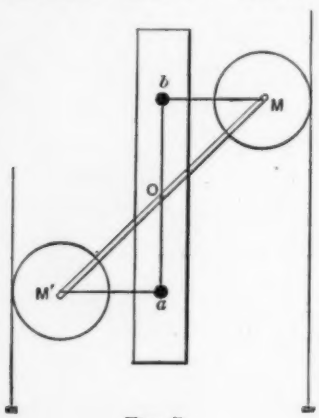

Fig. 7.

Next we have to find the horizontal distance between M and M' when in their positions for attracting, as in Fig. 7. This was done in three ways in order to be more free from mistake, as any error made is doubled. The first method was to use plumb-lines of quartz fibers set on the edges of the spheres of lead by means of a magnifying glass, and to measure their distance apart by means of a microscope mounted on the platform of a dividing engine. The second method was to measure OM and Ob accurately and calculate bM. These two ways were found equally good, and gave results agreeing to $\frac{1}{20}$ mm. The third way was to note the angle OMb which the pointer moved through, and knowing OM to calculate bM; but as the angle could not be observed as accurately as the distances, this third method was not used.

Three different distances bM were used with the same pair of attracting balls. They were 7.421, 5.565, and 3.714 cm.; they are nearly in the ratio of 4 : 3 : 2. The actual deflections of the little masses have to be subtracted; namely, 0.015, 0.025, and 0.069 cm., respectively, making the actual distances 7.406, 5.540, and 3.645 cm. If we now take the sum of the attractions of M for b, and M' for a, and subtract the sum of the attractions of M' for b, and M for a, we find that the resultant attractions should be as 1 : 2.05 : 5.25. The small masses were those described in the second series of experiments, and the large balls those described in the third. If we take as our error in the distance $2Mb$ a distance of $\frac{1}{10}$ mm., the error in Mb is one-half of this, and the error in the attraction will again double it, which gives us at most 1 in 400 for the shortest distance, and 1 in 800 for the longest.

The deflections were observed as before by means of a telescope and scale at a distance of 323 cm. from the mirror. In spite of all the precautions taken to prevent changes of temperature, the zero-point never remained absolutely steady, but shifted slowly. However, by taking a series of readings and using the average, this was obviated to a large extent; and the averages have a very close agreement, as will be seen. The following are the observed deflections for each of the distances: —

LEAST DISTANCE.

41.0	41.1	40.9	40.95	41.0
41.0	41.1	41.1	41.1	41.1
41.0	41.0	41.1	41.05	41.0
41.1	40.9	40.9	41.0	41.0
41.0	41.1	40.9	41.0	41.0
	41.1	41.1	41.0	40.9
	40.9	41.0	41.1	41.0
	41.1	41.0	41.1	41.1
	41.1	41.0	41.1	41.0
	41.0		40.9	40.95
Mean 41.02	41.04	41.00	41.03	41.00

Mean of all 41.02.

MEAN DISTANCE.

16.1	16.1	16.2
15.9	15.9	15.9
15.95	16.1	16.0
15.9	15.9	15.95
16.05	16.0	16.0
15.95	16.0	15.95
16.0	15.9	16.0
16.05	15.9	16.0
16.0	16.0	
Mean 15.99	15.98	16.00

Mean of all 15.99.

GREATEST DISTANCE.

7.8	7.8	7.9	7.7	7.9	7.7
7.7	7.6	7.6	7.9	7.65	7.9
7.8	8.0	7.9	7.8	7.85	7.8
7.75	7.7	7.7	7.9	7.8	7.7
7.8	7.8	7.8	7.8	7.8	7.8
7.8	8.0	7.8	7.7	7.8	7.75
7.8	7.7	7.7	7.8	7.8	7.8
7.7	7.9	7.8	7.85		7.75
7.9	7.7	7.8	7.8		7.7
7.65	7.8	7.8	7.7		
7.8	7.8	7.7	7.85		
7.8		7.8			
7.9		7.8			
7.7		7.8			
7.8		7.7			
7.8		7.8			
Mean 7.78	7.80	7.78	7.80	7.80	7.77

Mean of all 7.79

The number of readings at the mean distance was the last taken, and is not as great as for the other two on account of the instrument having been slightly disturbed by a blow; but the readings

are so consistent that they are sufficient. An attempt was now made to find the deflection due to the wires *cd* and *ef* alone, but it could not be done at all well. It seemed to be about 1 mm. for the nearest distance. This is about 1 part in 400, and as that is about the amount of error in the general method, the effect of the wires was neglected.

The tangents of twice the angles of deflections are then $\frac{7.79}{323}$, $\frac{15.99}{323}$, and $\frac{41.02}{323}$, and hence the angles of deflection are 82.84, 170.05, and 434.36, minutes respectively, which are in the ratio of 1 : 2.04 : 5.24. If we compare this with the calculated ratio 1 : 2.05 : 5.25, we find the agreement remarkably good, being out less than 1 part in 500 for the case of the greatest and least distances.

In conclusion, then, the law of Newton has been found to be true for the attractions of non-isotropic masses and for isotropic masses at distances apart as small as 3 or 4 cm.

Appendix.

To find the potential at a point outside a sphere made up of equidistant homogeneous disks, parallel to the plane of XY.

Let AB be a disk of radius b, z its vertical distance from the plane XY, $OP=r$, $COP=\theta$, $R=\sqrt{b^2+z^2}$; to find the potential at P, of a number of such disks which just make up the sphere.

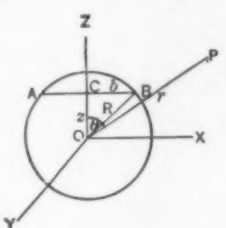

Fig. 8.

We have for the potential of a disk the equation

$$V=\frac{\pi\lambda}{r}\Big[(R^2-z^2)+(R^2-z^2)z\frac{P_1(\theta)}{r}+\tfrac{1}{2}\Big\{3\frac{R^2-z^2}{2}z^2-1\frac{R^4-z^4}{4}\Big\}\frac{P_2(\theta)}{r^2}$$

$$+\Big\{5\frac{R^2-z^2}{2}z^3-3\frac{R^4-z^4}{4}z\Big\}\frac{P_3(\theta)}{r^3}+\text{etc.}$$

$$+A\Big\{a_n\frac{R^2-z^2}{2}z^{2n}+a_{n-1}\frac{R^4-z^4}{4}z^{2n-2}+\text{etc.}+a_0\frac{R^{2n+2}-z^{2n+2}}{2n+2}\Big\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big],$$

where A is a constant, and a_n, a_{n-1}, $\cdots a_1$, a_0, are the coefficients of $P_{2n}(\theta)$ in the formula

$$P_{2n}(\theta)=\frac{1}{2^{n+1}}(a_n\mu^{2n}+a_{n-1}\mu^{2n-2}+\cdots+a_0)$$

The reason for using even harmonics will be seen presently.

Simplifying this expression, we have

$$V=\frac{\pi\lambda}{r}\Bigg[\{R^2-z^2\}\frac{P_0(\theta)}{r^0}+\{R^2z-z^3\}\frac{P_1(\theta)}{r}-\tfrac{1}{8}\{R^4-6R^2z^2+5z^4\}\frac{P_2(\theta)}{r^2}$$

$$+\text{etc.}+\frac{A}{2}\left\{\frac{a_n}{1}z^{2n}R^2+\frac{a_{n-1}}{2}z^{2n-2}R^4+\text{etc.}+\frac{a_0}{n+1}R^{2n+2}\right.$$

$$\left.-\left(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\right)z^{2n+2}\right\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Bigg],$$

where λ is the surface density.

Now we wish to sum up the separate potentials of a pile of such disks which make up a sphere.

Call the thickness of each disk $\equiv t$, and distance between any two consecutive ones $\equiv d$, and let there be m such disks on each side of the central one. In our problem m is very large, of the order of magnitude of the number of molecules in a unit of length. Using ρ for the volume density, we have $\lambda=\rho t$. Calling the vertical distances of the centers of the disks from the center of the sphere

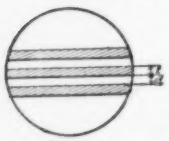

Fig. 9.

$$z_0,\ z_1,\ z_2,\ \cdots z_m,\ z_{-1},\ z_{-2},\ \cdots z_{-m},$$

we have

$$z_0=0,\ z_1=t+d,\ z_2=2(t+d),\ z_m=m(t+d),$$

$$z_{-1}=-(t+d),\ z_{-2}=-2(t+d),\ z_{-m}=-m(t+d),\ \text{etc.}$$

Substitute in V these values of z, and we get

$$z=0:dV=\frac{\pi\rho t}{r}\Bigg[R^2P_0(\theta)-\tfrac{1}{8}R^4\frac{P_2(\theta)}{r^2}+\text{etc.}$$

$$+\frac{A}{2}\cdot\frac{a_0}{n+1}R^{2n+2}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Bigg] \qquad (1)$$

$$z=t+d:dV=\frac{\pi\rho t}{r}\Big[\{R^2-(t+d)^2\}\frac{P_0(\theta)}{r^0}+\{R^2(t+d)-(t+d)^3\}\frac{P_1(\theta)}{r}$$
$$+\text{etc.}+\frac{A}{2}\Big\{\frac{a_n}{1}R^2(t+d)^{2n}+\frac{a_{n-1}}{2}R^4(t+d)^{2n-2}+\text{etc.}$$
$$+\frac{a_0}{n+1}R^{2n+2}-\Big(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\Big)(t+d)^{2n+2}\Big\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big]. \quad (2)$$

$$z=-(t+d):dV$$
$$=\frac{\pi\rho t}{r}\Big[\{R^2-(t+d)^2\}P_0(\theta)-\{R^2(t+d)-(t+d)^3\}\frac{P_1(\theta)}{r}+\text{etc.}$$
$$+\frac{A}{2}\Big\{\frac{a_n}{1}R^2(t+d)^{2n}+\frac{a_{n-1}}{2}R^4(t+d)^{2n-2}+\text{etc.}+\frac{a_0}{n+1}R^{2n+2}$$
$$-\Big(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\Big)(t+d)^{2n+2}\Big\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big]. \quad (3)$$

$$z=m(t+d):dV=\frac{\pi\rho t}{r}\Big[\{R^2-m^2(t+d)^2\}P_0(\theta)$$
$$+\{R^2m(t+d)-m^3(t+d)^3\}\frac{P_1(\theta)}{r}+\text{etc.}+\frac{A}{2}\Big\{\frac{a_n}{1}R^2m^{2n}(t+d)^{2n}$$
$$+\frac{a_{n-1}}{2}R^4m^{2n-2}(t+d)^{2n-2}+\text{etc.}+\frac{a_0}{n+1}R^{2n+2}$$
$$-\Big(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\Big)m^{2n+2}(t+d)^{2n+2}\Big\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big]. \quad (4)$$

$$z=-m(t+d):dV$$
$$=\frac{\pi\rho t}{r}\Big[\{R^2-m^2(t+d)^2\}P_0(\theta)-\{R^2m(t+d)-m^3(t+d)^3\}\frac{P_1(\theta)}{r}+\text{etc.}$$
$$+\frac{A}{2}\Big\{\frac{a_n}{1}R^2m^{2n}(t+d)^{2n}+\frac{a_{n-1}}{2}R^4m^{2n-2}(t+d)^{2n-2}+\text{etc.}+\frac{a_0}{n+1}R^{2n+2}$$
$$-\Big(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\Big)m^{2n+2}(t+d)^{2n+2}\Big\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big]. \quad (5)$$

Now when we go to sum, it is evident that the terms with odd harmonics disappear two and two, because they contain z to odd powers only; thus (2) and (3) cancel, (4) and (5), and so on. Using the symbol

$$_mS_r\equiv 1^r+2^r+3^r+\text{etc.}\cdots+m^r,$$

we have

$$\Sigma dV = V = \frac{\pi\rho t}{r}\Big[\{(2m+1)R^2 - 2\,{}_mS_2(t+d)^2\}P_0(\theta) + \text{etc.}$$

$$+ A\left\{-\left(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\right){}_mS_{2n+2}(t+d)^{2n+2}+\frac{a_n}{1}\,{}_mS_{2n}R^2(t+d)^{2n}+\text{etc.}\right.$$

$$\left.+\frac{a_0}{n+1}R^{2n+2}\right\}\frac{P_{2n}(\theta)}{r^{2n}}+\text{etc.}\Big].$$

Now $t+d=\frac{1}{m}R$, and if we call $t=\frac{1}{k}(t+d)$, then $t=\frac{1}{km}R$. Substituting these values, we get

$$V=\frac{\pi\rho}{kr}\left[\left\{\frac{2m+1}{m}-2\frac{{}_mS_2}{m^3}\right\}R^2P_0(\theta)+\text{etc.}\right.$$

$$+A\left\{-\left(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\right)\frac{{}_mS_{2n+2}}{m^{2n+3}}+\frac{a_n}{1}\frac{{}_mS_{2n}}{m^{2n+1}}+\text{etc.}+\frac{a_0}{n+1}\,\frac{1}{m}\right\}$$

$$\left.\frac{P_{2n}(\theta)}{r^{2n}}R^{2n+3}+\text{etc.}\right].$$

Now (from Todhunter's Algebra, p. 415) the term of ${}_mS_r$ with the highest power of m is $\frac{1}{r+1}m^{r+1}$, but all the coefficients of the general term of the last equation are of the form

$$\frac{1}{m^{r+1}}\,{}_mS_r=\frac{1}{r+1}+A\frac{1}{m}+B\frac{1}{m^2}+\text{etc.}$$

Hence the only part of that term which is of the first order of magnitude is

$$A\left\{-\frac{\left(\frac{a_n}{1}+\frac{a_{n-1}}{2}+\text{etc.}+\frac{a_0}{n+1}\right)}{2n+3}+\frac{\frac{a_n}{1}}{2n+1}+\frac{\frac{a_{n-1}}{2}}{2n}+\text{etc.}+\frac{\frac{a_0}{n+1}}{1}\right\},$$

which can be written

$$A\left\{\frac{a_n}{2n+1}+\frac{a_{n-1}}{2n-1}+\text{etc.}+\frac{a_1}{3}+\frac{a_0}{1}\right\}\frac{2}{2n+3}.$$

From Todhunter's "Functions of Laplace, Lamé, and Bessel," p. 17, we have

$$\frac{1}{2^{n+1}}\left(\frac{a_n}{k+2n+1}+\frac{a_{n-1}}{k+2n-1}+\text{etc.}+\cdots\right)=\frac{k(k-2)(k-4)\cdots(k-2n+2)}{(k+2n+1)(k+2n-1)\cdots(k+1)},$$

where k has any positive value. Let $k=0$; then

$$\frac{a_n}{2n+1}+\frac{a_{n-1}}{2n-1}+\text{etc.}+\frac{a_1}{3}+\frac{a_0}{1}=0,$$

or the part of the coefficients of the harmonics that is of the first order is zero in every case, and V can only have terms in the spherical harmonics of the form $\left(\frac{A}{m}+\frac{B}{m^2}+\text{etc.}\right)P^2{}_n(\theta)$. Hence, neglecting terms which are not of the first order of magnitude, our equation for V reduces to

$$V=\frac{\pi\rho}{kr}\left[\frac{2m+1}{m}-2\frac{{}_mS_2}{m^3}\right]R^3=\frac{\pi\rho}{kr}\left[2+\frac{1}{m}-\frac{1}{3}\frac{m(m+1)(2m+1)}{m^3}\right]R^3.$$

Or again, neglecting $\frac{1}{m}$, $\frac{1}{m^2}$, etc.,

$$V=\frac{\pi\rho}{kr}\frac{4}{3}R^3=\frac{1}{k}\cdot\frac{4}{3}\frac{\pi R^3\rho}{r},$$

which is the potential of such a sphere as ordinarily given, assuming the mass $\frac{1}{k}$ of what it would be were it solid.

Hence no terms in θ enter of the first order of magnitude.

BRYN MAWR COLLEGE, BRYN MAWR, PA.,
June, 1894.

THE INFLUENCE OF TEMPERATURE UPON THE TRANSPARENCY OF SOLUTIONS.

BY EDWARD L. NICHOLS AND MARY C. SPENCER.

THE experiments to be described in this paper deal with the transparency of certain aqueous solutions, for various wave-lengths of the visible spectrum and at temperatures ranging between 20° and 80° C. For the purposes of these measurements the horizontal slit photometer was used. The instrument was mounted upon a track, at the ends of which two similar incandescent lamps were placed. These lamps were so adjusted as to give as nearly as possible the same quality of light, and in front of one of them, at the observer's right hand, was placed a cell containing the solution to be tested. In Fig. 1, which shows the

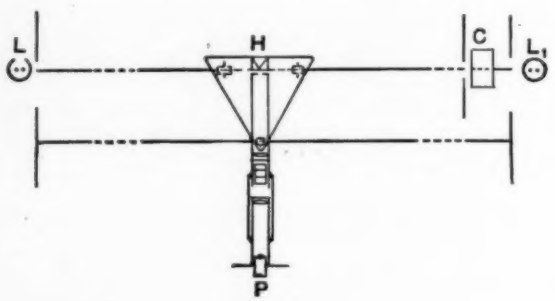

Fig. 1.

arrangement of the apparatus, L and L_1 are the lamps, C is the cell containing the solution, and HP is the spectrophotometer.[1]

Figure 2 gives a cross-section of the cell used for heating the solutions, the transmitting power of which was to be tested. It consisted of a cylinder of brass about 15 cm. in diameter. This

[1] For a description of the horizontal-slit photometer see Transactions of the American Institute of Electrical Engineers, 1890; also PHYSICAL REVIEW, Vol. 2, p. 138.

cylinder was provided with broad flanges on either end, against which sheets of thin plate glass were securely clamped. A neck in the top of the cylinder allowed of the introduction of the solution and also of the insertion of a thermometer. The distance between the outer faces of the cell was 8.9 cm., and the thickness of the contained layer of liquid 8.5 cm.

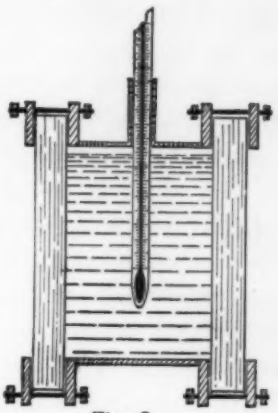

Fig. 2.

The cell was heated by means of an electric current which traversed a coil of wire surrounding the brass cylinder. This coil is not shown in the diagram.

The method of procedure was as follows:—

The observing telescope of the photometer was set so as to bring a given portion of the visible spectrum into the field of view, and readings were made of the positions upon the bar at which the region under inspection was equally bright in the spectra of the two lamps. The cell containing the solution was then interposed and the light ratio was redetermined. A series of readings was taken in this way for the wave-length in question, the temperature of the solution being varied from time to time. The results of these observations were then indicated by means of a curve in which ordinates represented transmitting powers and abscissas temperatures, and the process was repeated until a series of such curves, for different regions of the spectrum, had been obtained. From these it was possible to derive the data for the construction of other curves showing the relative distribution of energy in the absorption spectrum of the solution at any desired temperature within the range covered by the experiment.

It is evident that the method just outlined will give much more definite and precise information concerning the influence of temperature upon the transparency of a solution than it is possible to obtain by means of the methods pursued by previous observers. Although a considerable amount of information upon this subject

had already been massed by Gladstone,[1] Melde,[2] Hartley,[3] Conroy,[4] and others, all of whom agree in the general statement that temperature lessens the power of transmitting light, no one, so far as the present writers are aware, had undertaken to determine quantitatively, wave-length by wave-length, degree by degree, the exact amount of this decrease. This, by means of the apparatus just described, the writers have been able to do in the case of a considerable number of solutions.

The solutions tested were for the most part colored salts dissolved in distilled water, the concentration being such as to allow an easily measurable quantity of light to be transmitted, but at the same time to show distinctly the character of the selective absorption, where such existed. An equally important field, that of the study of the influence of temperature upon colorless solutions possessing definite absorption bands of great density (as, for example, the solutions of the salts of the rare earths), was not included in our investigation.

Several modes of expressing the results obtained by the method just indicated suggest themselves. One may, for example, give the transmitting power of the cell containing each of the solutions studied, in terms of that of the same cell when filled with distilled water and subjected to the same temperature changes; or, having determined the loss by reflection and by absorption within the glass walls of the cell, one may reduce the transparency in each case to that of a layer of unit thickness. For the purposes of the present investigation it was deemed sufficient to give the transmission of the filled cell in each case, since it was the comparison of the transmitting power of the solution when cold with that which it possessed at higher temperatures which was desired.

The substances tested were distilled water and aqueous solutions, chiefly of various salts. These, grouped according to their behavior when heated, are given in the following list: —

[1] Gladstone, Philosophical Magazine (4), Vol. 14, p. 423.
[2] Melde, Annalen der Physik und Chemie, Vol. 126, p. 284.
[3] Hartley, Proceedings of the Royal Society, Vol. 22, p. 241.
[4] Conroy, Philosophical Magazine (5), Vol. 31, p. 371.

(A) Cobalt-ammonium sulphate,
Potassium bichromate.

(B) Potassium chromate,
Sodium bichromate,
Copper sulphate,
Chromic sulphate,
Potassium ferric cyanide.

(C) Distilled water,
Cochineal,
Sodium nitrate,
Nickel sulphate.

(D) Copper acetate,
Ferric chloride,
Potassium permanganate,
Copper chloride,
Nickel chloride.

Measurements at a single temperature were also made with the empty cell interposed between the spectrophotometer and the source of light, with results which are given in Table I.

TABLE I.

TRANSPARENCY OF THE EMPTY CELL.

Wave-length	0.6867 μ	0.5896	0.4700 μ	0.4080 μ
Transmission	0.709	0.763	0.783	0.785

Experiments upon the substances of Group C having shown the influence of heat upon the transmitting power of the filled cell to be inappreciable, it was deemed unnecessary to make measurements with the empty cell at high temperatures.

The quantity denoted by the term "transmission" in the above, and in all subsequent tables, is the ratio of the light reaching the photometer through the cell to that which reaches the instrument directly when the cell is withdrawn.

The results of our measurements upon the solutions of the preceding list are contained in the following tables, and they are indicated graphically in some cases by means of the two species of diagram already referred to.

The first of these is an isochromatic curve showing the change in transmitting power of a single wave-length with varying temperature; the other is an isothermal curve by means of which the distribution of transparency in the visible spectrum is given for a single temperature.

It will be seen from the following tables that the solutions tested fall naturally into the four groups already given : —

(1) Solutions suffering *temporary* change of transmitting power throughout the spectrum when heated (Group A).

(2) Solutions suffering *temporary* decrease of transparency in certain regions, but not throughout the entire spectrum (Group B).

(3) Liquids unaffected as regards transparency by temperature changes up to 80° (Group C).

(4) Solutions suffering *permanent* change of color as the result of heating (Group D). Such solutions do not return to their original condition when cooled.

Measurements upon Group D were made only for a single region of the spectrum. It will be seen that as a rule they suffer diminution of transmitting power with rise of temperature. This sometimes occurs continuously, but with increasing rapidity, as in the cases of ferric chloride and copper chloride, while sometimes a sudden and very marked falling off of transparency occurs at a definite temperature, as in the case of copper acetate and nickel chloride. One of the solutions of this group, potassium permanganate, gains materially in transparency for the wave-length tested, a result due to a gradual decomposition brought about by heating.

GROUP A.

Solutions showing temporary loss throughout the spectrum.

TABLE II.

COBALT AMMONIUM SULPHATE (8 GRMS. IN 300 CC. H_2O).

	Wave-length 0.6867 μ.						
Temperature	18°	28°	38°	48°	59°	69°	78°
	22°	31°	42°	56°	64°	74°	82°
Transmission	0.76	0.76	0.69	0.68	0.65	0.64	0.61
	Wave-length 0.5896 μ.						
Temperature	19°	25°	38°	48°	58°	68°	78°
	23°	33°	42°	52°	61°	72°	81°
Transmission	0.58	0.57	0.56	0.56	0.52	0.51	0.50

TABLE II. (*continued*).

Wave-length 0.5500 μ.							
Temperature	20°	30°	39° / 38°	49° / 50°	60°	71°	80°
Transmission	0.21	0.20	0.19	0.19	0.17	0.15	0.15
Wave-length 0.5200 μ.							
Temperature	20°	31°	40°	50°	60°	69°	80°
Transmission	0.07	0.06	0.06	0.05	0.05	0.05	0.04
Wave-length 0.4900 μ.							
Temperature	21°	30°	40°	49°	61°	69°	80°
Transmission	0.07	0.067	0.05	0.06	0.06	0.05	0.05
Wave-length 0.4700 μ.							
Temperature	20°	31°	40°	49°	60°	70°	80°
Transmission	0.14	0.12	0.11	0.10	0.10	0.10	0.10
Wave-length 0.4550 μ.							
Temperature	22°	30°	39°	50°	60°	69°	80°
Transmission	0.08	0.07	0.07	0.07	0.06	0.05	0.05

The above results for cobalt ammonium sulphate, which may be regarded as typical, are indicated graphically by means of both forms of diagram in Fig. 3.

In this and in all solutions tested, excepting those which suffered permanent change as the result of heating, the isochromatic diagrams (within the limits of accuracy) *were straight lines.*

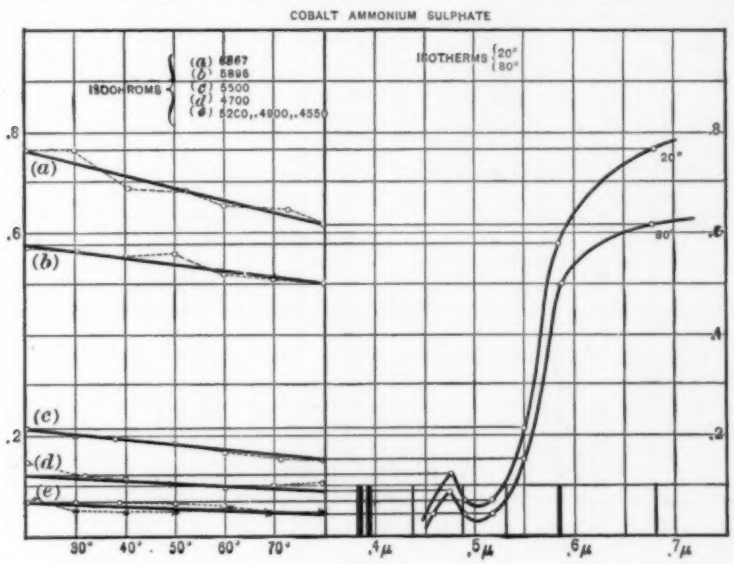

Fig. 3.

TABLE III.

POTASSIUM BICHROMATE (4 GRMS. IN 300 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	20°	29°	40°	50°	60°	69°	79°
Transmission	0.76	0.75	0.74	0.73	0.72	0.71	0.69
Wave-length 0.6200 μ.							
Temperature	21°	31°	41°	51°	59°	69°	80°
Transmission	0.89	0.85	0.85	0.89	0.84	0.85	0.85
Wave-length 0.5650 μ.							
Temperature	20°	26°	31°	38°	50°	60°	70°	79°
Transmission	0.66	0.64	0.64	0.63	0.58	0.54	0.53	0.52
Wave-length 0.5600 μ.							
Temperature	20°	30°	40°	50°	60°	69°	79°
Transmission	0.44	0.44	0.40	0.38	0.35	0.32	0.28
Wave-length 0.5500 μ.							
Temperature	21°	30°	39°	50°	58°	70°	79°
Transmission	0.18	0.17	0.15	0.12	0.10	0.09	0.09
Wave-length 0.5375 μ.							
Temperature	20°	29°	43°	50°	60°	70°	80°
Transmission	0.11	0.10	0.09	0.08	0.07	0.06	0.00

Isotherms of potassium bichromate, for 20° and 80° respectively, are given in Fig. 4.

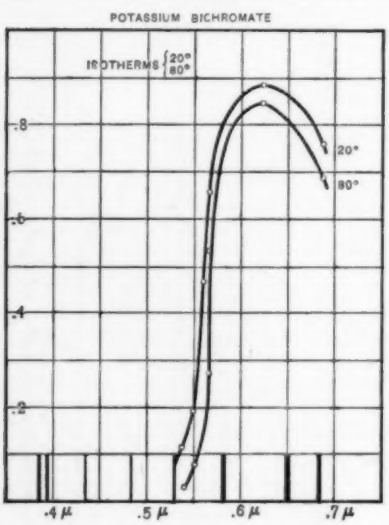

Fig. 4.

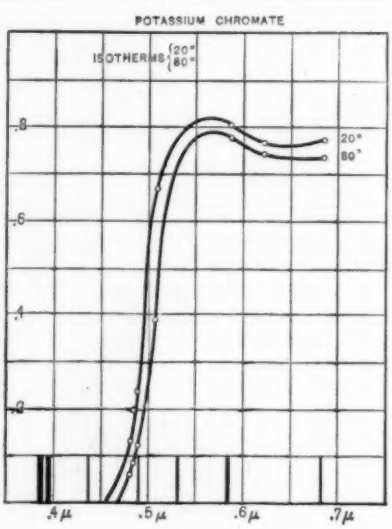

Fig. 5.

TABLE IV.

POTASSIUM CHROMATE[1] (4 GRMS. IN 300 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	21°	28°	40°	49°	60°	69°	80°
Transmission	0.78	0.78	0.77	0.75	0.76	0.76	0.72
Wave-length 0.6200 μ.							
Temperature	21°	31°	42°	50°	60°	70°	80°
Transmission	0.76	0.78	0.77	0.77	0.75	0.76	0.76
Wave-length 0.5896 μ.							
Temperature	27°	39°	47°	54°	60°	65°	73°	82°
Transmission	0.80	0.80	0.79	0.79	0.77	0.79	0.79	0.77
Wave-length 0.5050 μ.							
Temperature	20°	33°	42°	53°	59°	70°	78°	84°
Transmission	0.63	0.63	0.61	0.50	0.50	0.43	0.39	0.36
Wave-length 0.4900 μ.							
Temperature	20°	28°	40°	46°	58°	65°	76°
Transmission	0.23	0.21	0.21	0.19	0.19	0.16	0.13
Wave-length 0.4860 μ.							
Temperature	22°	29°	48°	62°	73°	82°
Transmission	0.20	0.18	0.13	0.11	0.09	0.08
Wave-length 0.4800 μ.							
Temperature	24°	46°	59°	70°	75°
Transmission	0.12	0.10	0.09	0.07	0.00

Isotherms of potassium chromate, for 20° and 80° respectively, are given in Fig. 5.

[1] Potassium chromate forms an intermediate member of Groups A and B. In one of the regions explored (0.6200 μ – 0.5900 μ), the influence of temperature was almost imperceptible.

GROUP B.

Solutions showing temporary loss throughout a portion of the spectrum.

TABLE V.

SODIUM BICHROMATE (4 GRMS. IN 450 CC. H_2O).

	Wave-length 0.6867 μ.						
Temperature	22°	30°	40°	50°	60°	69°	80°
Transmission	0.74	0.78	0.80	0.78	0.72	0.73	0.74
	Wave-length 0.6200 μ.						
Temperature	22°	29°	39°	50°	59°	69°	80°
Transmission	0.82	0.83	0.83	0.83	0.83	0.84	0.83
	Wave-length 0.5896 μ.						
Temperature	20°	30°	40°	50°	59°	70°	80°
Transmission	0.71	0.71	0.73	0.71	0.72	0.71	0.71
	Wave-length 0.5500 μ.						
Temperature	21°	30°	40°	50°	60°	70°	79°
Transmission	0.51	0.48	0.47	0.44	0.41	0.38	0.37
	Wave-length 0.5350 μ.						
Temperature	22°	30°	39°	49°	59°	71°	80°
Transmission	0.13	0.11	0.10	0.09	0.08	0.09	0.07
	Wave-length 0.5230 μ.						
Temperature	21°	29°	39°	49°	61°	70°	79°
Transmission	0.10	0.09	0.08	0.08	0.07	0.06	0.05

Isotherms of sodium bichromate, for 20° and 80° respectively, are given in Fig. 6.

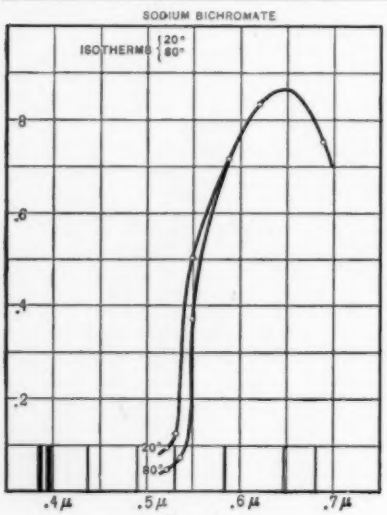

Fig. 6.

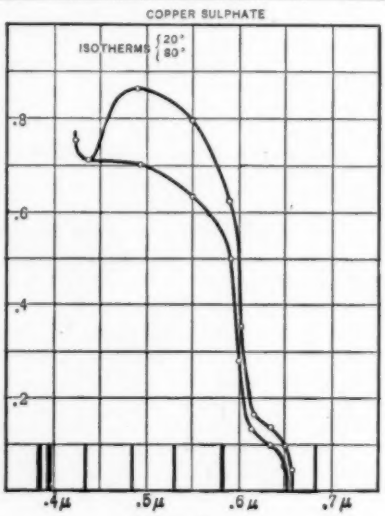

Fig. 7.

TABLE VI.

COPPER SULPHATE (8 GRMS. IN 300 CC. H_2O).

Wave-length 0.6550 μ.							
Temperature			20°		30°		47°
Transmission			0.06		0.01		0.008
Wave-length 0.6500 μ.							
Temperature	20°	30°	40°	52°	60°	70°	78°
Transmission	0.10	0.09	0.08	0.08	0.07	0.07	0.06
Wave-length 0.6300 μ.							
Temperature	21°	29°	40°	49°	60°	69°	77°	81°
Transmission	0.16	0.15	0.15	0.13	0.12	0.11	0.11	0.11
Wave-length 0.6200 μ.							
Temperature	21°	30°	41°	51°	59°	69°	81°
Transmission	0.19	0.17	0.16	0.15	0.15	0.14	0.13
Wave-length 0.6000 μ.							
Temperature	20°	30°	40°	50°	60°	70°	80°
Transmission	0.36	0.34	0.34	0.32	0.32	0.30	0.30
Wave-length 0.5896 μ.							
Temperature	21°	31°	40°	51°	59°	71°	80°
Transmission	0.63	0.60	0.56	0.53	0.52	0.52	0.51
Wave-length 0.5500 μ.							
Temperature	21°	30°	39°	52°	60°	69°	81°
Transmission	0.80	0.80	0.72	0.72	0.69	0.67	0.65
Wave-length 0.4900 μ.							
Temperature	21°	30°	40°	49°	59°	70°	80°
Transmission	0.85	0.81	0.82	0.80	0.78	0.76	0.76
Wave-length 0.4350 μ.							
Temperature	20°	32°	40°	50°	60°	70°	80°
Transmission	0.71	0.71	0.71	0.70	0.73	0.73	0.73
Wave-length 0.4250 μ.							
Temperature	22°	30°	40°	50°	59°	70°	79°
Transmission	0.76	0.74	0.75	0.75	0.76	0.77	0.75

Isotherms of copper sulphate, for 20° and 80° respectively, are given in Fig. 7.

TABLE VII.

CHROMIC SULPHATE (7 GRMS. IN 800 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	22°	30°	40°	49°	61°	69°	79°
Transmission	0.52	0.50	0.49	0.49	0.48	0.44	0.43
Wave-length 0.6200 μ.							
Temperature	20°	29°	39°	49°	59°	71°	80°
Transmission	0.25	0.24	0.24	0.23	0.22	0.22	0.21
Wave-length 0.5896 μ.							
Temperature	21°	29°	30°	39°	60°	70°	79°
Transmission	0.13	0.12	0.12	0.11	0.11	0.10	0.10
Wave-length 0.5500 μ.							
Temperature	20°	30°	39°	50°	60°	69°	80°
Transmission	0.14	0.14	0.13	0.13	0.12	0.12	0.12
Wave-length 0.5200 μ.							
Temperature	22°	30°	41°	51°	60°	70°	80°
Transmission	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Wave-length 0.4700 μ.							
Temperature	20°	31°	40°	50°	60°	70°	80°
Transmission	0.56	0.56	0.56	0.54	0.50	0.47	0.44
Wave-length 0.4350.							
Temperature	22°	30°	40°	50°	59°	71°	80°
Transmission	0.45	0.43	0.43	0.42	0.42	0.39	0.38

Isotherms of chromic sulphate, for 20° and 80° respectively, are given in Fig. 8.

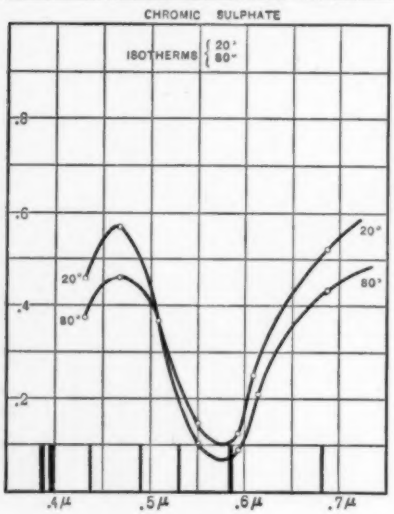

Fig. 8.

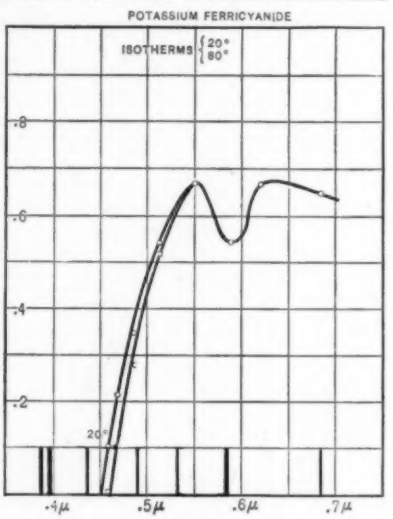

Fig. 9.

TABLE VIII.

POTASSIUM FERRICYANIDE (4 GRMS. IN 150 CC. H_2O).

Wave-length 0.6876 μ.							
Temperature	24°	30°	44°	58°	69°	80°	
Transmission	0.61	0.64	0.64	0.64	0.64	0.63	
Wave-length 0.6200 μ.							
Temperature	20°	32°	39°	49°	60°	70°	80°
Transmission	0.69	0.62	0.67	0.66	0.67	0.69	0.67
Wave-length 0.5896 μ.							
Temperature	22°	35°	54°	62°	69°	78°	
Transmission	0.54	0.55	0.54	0.53	0.54	0.54	
Wave-length 0.5500 μ.							
Temperature	20°	32°	40°	49°	59°	69°	81°
Transmission	0.67	0.68	0.67	0.67	0.68	0.67	0.67
Wave-length 0.5200 μ.							
Temperature	22°	38°	45°	55°	64°	74°	
Transmission	0.59	0.56	0.56	0.56	0.56	0.53	
Wave-length 0.4900 μ.							
Temperature	20°	31°	41°	51°	60°	69°	80°
Transmission	0.36	0.33	0.32	0.31	0.30	0.29	0.29
Wave-length 0.4700 μ.							
Temperature	21°	41°	53°	66°	75°	82°	
Transmission	0.19	0.17	0.16	0.13	0.11	0.10	
Wave-length 0.4625 μ.							
Temperature	20	40°	52°	63°	70°		
Transmission	0.12	0.07	0.07	0.06	0.00		

Isotherms of potassium ferricyanide, for 20° and 80° respectively, are given in Fig. 9.

GROUP C.

Liquids unaffected by change of temperature.

TABLE IX.

DISTILLED WATER.

Wave-length 0.6867 μ.							
Temperature	22°	30°	40°	50°	60°	70°	80°
Transmission	0.82	0.82	0.83	0.83	0.83	0.83	0.83
Wave-length 0.5200 μ.							
Temperature	22°	29°	40°	49°	59°	69°	80°
Transmission	0.72	0.73	0.72	0.72	0.71	0.71	0.71
Wave-length 0.4250 μ.							
Temperature	20°	30°	40°	50°	60°	70°	80°
Transmission	0.81	0.82	0.81	0.82	0.82	0.83	0.82

TABLE X.

COCHINEAL (3 GRMS. IN 600 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	23°	31°	41°	49°	59°	70°	80°
Transmission	0.76	0.76	0.76	0.75	0.75	0.75	0.76
Wave-length 0.6200 μ.							
Temperature	20°	30°	40°	50°	60°	70°	80°
Transmission	0.33	0.35	0.34	0.34	0.35	0.34	0.34
Wave-length 0.5896 μ.							
Temperature	22°	30°	40°	50°	60°	70°	80°
Transmission	0.18	0.17	0.17	0.16	0.16	0.17	0.17
Wave-length 0.5350 μ.							
Temperature	20°	30°	40°	50°	59°	70°	80°
Transmission	0.40	0.41	0.40	0.39	0.39	0.40	0.40

TABLE XI.

SODIUM NITRATE (4 GRMS. IN 300 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	20°	30°	40°	50°	61°	70°	79°
Transmission	0.78	0.79	0.79	0.80	0.80	0.80	0.80
Wave-length 0.5500 μ.							
Temperature	20°	30°	40°	50°	60°	70°	80°
Transmission	0.88	0.88	0.86	0.86	0.84	0.84	0.86
Wave-length 0.4350 μ.							
Temperature	20°	30°	40°	50°	60°	70°	80°
Transmission	0.84	0.85	0.85	0.82	0.83	0.82	0.82

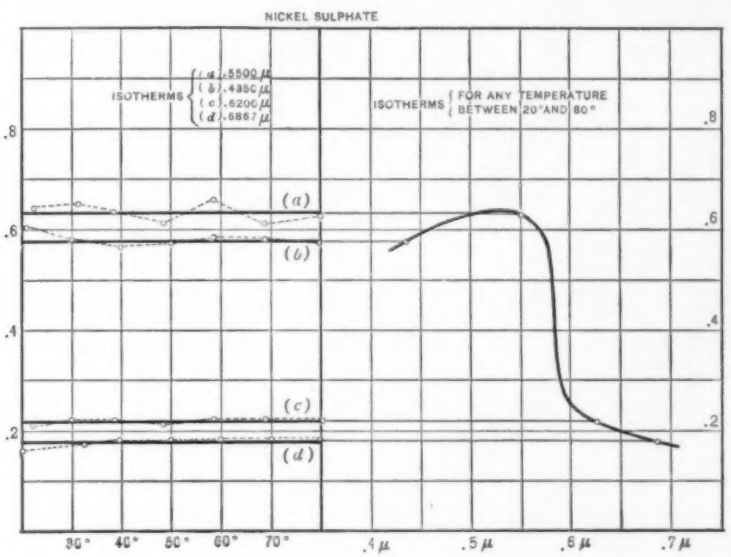

Fig. 10.

TABLE XII.

NICKEL SULPHATE (4 GRMS. IN 300 CC. H_2O).

Wave-length 0.6867 μ.							
Temperature	20°	32°	40°	50°	60°	70°	80°
Transmission	0.17	0.18	0.19	0.19	0.19	0.19	0.19

TABLE XII. (*continued*).

Wave-length 0.6200 μ.							
Temperature	23°	30°	39°	49°	59°	69°	81°
Transmission	0.21	0.22	0.22	0.21	0.22	0.22	0.22
Wave-length 0.5500 μ.							
Temperature	22°	31°	39°	49°	59°	69°	80°
Transmission	0.64	0.65	0.63	0.61	0.66	0.61	0.62
Wave-length 0.4350 μ.							
Temperature	21°	30°	40°	50°	59°	69°	80°
Transmission	0.61	0.58	0.57	0.58	0.59	0.59	0.58

A typical example of Group C, in which the isochroms are all horizontal straight lines is nickel sulphate, the characteristics of which are indicated by both forms of diagram in Fig. 10. The observational errors, always large in colorimetric work, are more than usually prominent in this case, particularly in the region 0.55 μ, but it is evident from the diagram that in none of the regions studied is the transparency of nickel sulphate modified to a determinable degree by change of temperature.

GROUP D.

Solutions suffering permanent change of color as the result of heating.

TABLE XIII.

COPPER ACETATE (4 GRMS. IN 300 CC. H_2O).

Temperature	22°	30°	39°	50°	60°	70°	80°	$\lambda = 0.550\ \mu$.
Transmission	0.52	0.51	0.48	0.46	0.42	0.40	0.00	

TABLE XIV.

FERRIC CHLORIDE (4 GRMS. IN 150 CC. H_2O).

Temperature	24°	38°	41°	50°	60°	$\lambda = 0.505\ \mu$.
Transmission	0.15	0.14	0.13	0.07	0.00	

TABLE XV.

POTASSIUM PERMANGANATE (1 GRM. IN 1000 CC. H_2O).

Temperature	20°	30°	40°	50°	59°	69°	80°	$\lambda = 0.620\ \mu$.
Transmission	0.27	0.35	0.37	0.39	0.41	0.42	0.49	

TABLE XVI.

COPPER CHLORIDE (4 GRMS. IN 300 CC. H_2O).

Temperature	21°	29°	40°	50°	60°	$\lambda = 0.470\ \mu$.
Transmission	0.61	0.58	0.54	0.43	0.00	

TABLE XVII.

NICKEL CHLORIDE (4 GRMS. IN 300 CC. H_2O).

Temperature	20°	30°	40°	50°	60°	$\lambda = 0.550\ \mu$.
Transmission	0.12	0.12	0.11	0.09	0.00	

The results of the above measurements upon Group D are embodied in the diagrams of Fig. 11.

With reference to the results given in numerical and graphical form in this paper, it is probably not without significance to note that in general the influence of a rise of temperature upon the color of pigments and of solutions is the same. The tendency in both cases is towards increased absorption, the loss of transmitting power being selective rather than of uniform distribution throughout the visible spectrum. It is of interest, moreover, to note from Table IX. that water itself suffers no loss of transparency and no appreciable change of color when heated.

From a more detailed study of various solutions, especially of the group considered last, much that is interesting and important might doubtless be derived. The importance, likewise, of making measurements of this character upon solutions possessing definite absorption bands, to which reference has been made in a previous paragraph, is obvious. The investigation might be extended with

great interest also to the infra-red and to the ultra-violet, in which important regions of the spectrum the transmitting power of very many substances, so far as quantitive measurements are concerned, to say nothing of the influence of temperature upon that

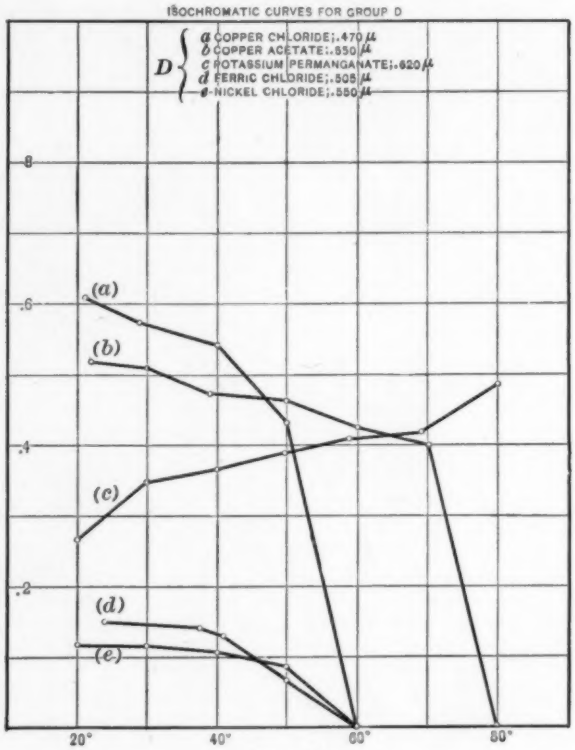

Fig. 11.

property, remains as yet unknown. If the incomplete experiments described here serve to indicate, even dimly, the direction to be given to further research in this field, the publication of them will have fulfilled its purpose.

AUGUST, 1894.

DETERMINATION OF THE ELECTRIC CONDUCTIVITY OF CERTAIN SALT SOLUTIONS.

By Albert C. MacGregory.

Introduction.

DURING the last few years a great deal of work has been done in the line of determining the electric conductivity of certain salts in their water solutions. Two objects are accomplished by means of such observations; namely, the determination of the velocities of the so-called ions, and the gaining of some insight into the condition of the salts when in solution. It is true that the same objects may be accomplished by observations of the depression of the freezing-point, but owing to the ease and accuracy of making the observations, the following method seems to be preferable.

The following determinations fill in a few vacancies in the list of results heretofore obtained for salts of the alkaline earths and acetates.

Apparatus.

The resistance bottles used were the same as those employed by Professor Kohlrausch in his work.

As the solutions varied in strength from $m=0.0001$ to $m=1.00$ (m denotes the gram equivalent in the liter of solution), it was necessary to employ two resistance bottles, one for the solutions from $m=0.0001$ to $m=0.01$, and the other for the remaining ones.

In measuring the most dilute solutions I employed a Becher glass of 80 mm. diameter and 130 mm. high: the edge was ground off even and fitted with a hard rubber cover 10 mm. thick and 110 mm. across. By means of three small pieces of rubber on the under side all lateral movement was avoided. Three holes were bored through the cover: two of them were situated on either

side of the center at a distance of 25 mm. from the same, and through them passed heavy copper wires. At the upper end of these wires binding posts were placed, while at the lower end were fastened large platinum wires ending in the electrodes of heavy platinum foil, 40 mm. square. The wire and foil were fastened together by welding and soldering, and were afterwards platinized in the usual manner. The third hole contained the thermometer, which entered the solution midway between the electrodes on a line connecting the outer edge.

With a normal filling of 500 cc. the electrodes dipped about 20 mm. under the surface of the liquid. The glass was entirely surrounded by felt.

The thermometer used was graduated to 0.°2, thus giving readings to 0.02°. The thermometer was tested by comparison with one from the Reichsanstalt. The bottle used for the other solutions consisted of two small glass bottles joined by a tube about 6 mm. in diameter. The bottles were provided with glass stoppers. After being filled, the bottle was placed in a water bath and the thermometer hung next to the connecting tube. Owing to the heat produced by the passage of the current the bridge readings were made as rapidly as possible. It was always necessary to wait until the temperature of the solution was the same as that of the bath before the readings were taken. The Kohlrausch roller bridge which was used was supplied with resistances of 1, 10, 100, and 1000 ohms, but for the most part only the 100 and the 1000 were used, their actual value being carefully determined by comparison with a normal instrument. By the use of a rheostat having resistances up to 4000 ohms the bridge wire was calibrated for every $\frac{1}{100}$ of its length. Whenever it was possible the resistances were determined by the use of both the 100 and 1000 ohms, and the middle taken as the true value. If the two values did not agree within 0.2 per cent, the bridge was again calibrated. Twelve calibrations in all were made during the course of the work. At one end of the wire the corrections remained quite constant, while at the other end there was a variation between the beginning to the completion of my work equivalent to about 0.0005 of the entire length of the wire.

Resistance Capacity of the Bottles.

The resistance capacities of the two bottles were determined by the use of normal and part normal solutions of KCl and NaCl. Before the solutions were used they were carefully tested by comparing their conductivity and specific gravity with existing data.

The capacity of the larger bottle was found by the use of solutions having a strength $m=0.05$, $m=0.02$, $m=0.01$, the conductivity of these solutions at 18° being, according to Kohlrausch, 5415, 2246, and 1147 respectively for KCl, and 4485, 1876, and 962 for NaCl (Hg. = 1). These values are to be multiplied by 10^{-10}. For the solutions used in calibrating the smaller bottle the values of m were 1.00, 0.5, and 0.1.

The mercury capacities thus found for the larger bottle were as follows:—

Salt	$m=$ 0.05	0.02	0.01
NaCl	1073.9	1072.5	1073.2
KCl.	1071.0	1075.0	1073.0

Middle $1073 \cdot 10^{-8}$ ohms.

For the smaller bottle:—

Salt	$m=$ 1.00	0.5	0.1
KCl.	1652.4	1653.0	1650.1
NaCl	1650.7	1651.3	1653.0

Middle $1651.7 \cdot 10^{-6}$ ohms.

Making the Solutions.

Whenever it was possible the solutions were made by weighing out the required amount of the pure salt, dissolving it in water, and then diluting to a liter of solution. When this was not possible, a concentrated solution was made and then brought to the normal strength by the specific gravity method. To accomplish this it was necessary to use tables giving the relation between the specific gravity and the per cent of salt. The following tables

were used: from Kohlrausch for $SrCl_2$ and $Ca(NO_3)_2$, from Franz for $Ba(C_2H_3O_2)_2$, and from Hager for $Ca(C_2H_3O_2)_2$.

The normal solutions thus obtained were tested by comparing with tables of the specific gravity from other authors, and, when possible, with tables of the electric conductivity.

The values thus found for the specific gravity of the normal solutions were as follows: —

Salt.	Sp. Grav. $\frac{18}{4}$.	Salt.	Sp. Grav. $\frac{18}{4}$.
$\frac{1}{2}$ $CaCl_2$	1.0435	$\frac{1}{2}$ $SrCl_2$	1.06765
$\frac{1}{2}$ $Ca(NO_3)_2$	1.0611	$\frac{1}{2}$ $Sr(NO_3)_2$	1.0816
$\frac{1}{2}$ $Ca(C_2H_3O_2)_2$	1.0386	$\frac{1}{2}$ $Sr(C_2H_3O_2)_2$	1.0669
$\frac{1}{2}$ $Ba(C_2H_3O_2)_2$	1.0843	$\frac{1}{2}$ $K_2C_2O_4$	1.0575

The solutions of $m=0.5$ to $m=0.05$ were made by diluting the normal solutions in quantities of 100 cc. (The smaller bottle held about 40 cc.) For the more dilute solutions I used a method suggested by Professor Kohlrausch,[1] which is as follows: The Becher glass was first filled with 500 cc. of water and its conductivity determined. Then I drew out 9.5 cc. of water, and using very exact pipettes added successively 0.5 cc., 0.5 cc., 2.0 cc., and 2.0 cc., of the solution for which $m=0.1$, determining the conductivity after each addition. Then 0.5 cc., 2.0 cc., and 2.0 cc. of the solution for which $m=1.0$ were added in the same way. After each addition the pipettes were rinsed out three or four times.

In this manner I obtained solutions having the following strengths: —

After the addition of the solution $m=0.1$:—

0.5 cc.	$m = 0.0001018$
0.5	0.0002034
2.0	0.0006079
2.0	0.0010090

From solution $m=1.0$: —

0.5 cc.	$m = 0.002016$
2.0	0.006024
2.0	0.010000

[1] Wied. Ann. XXVI., 175, 1885.

The conductivity was determined for eleven (11) degrees of concentration between the values $m = 1.0$ and $m = 0.0001$.

In order to compute the molecular conductivity from the conductivity of the solution, the latter was diminished by the conductivity of the water, and this difference was divided by the values for m as given above.

As the resistance in the Becher glass depended upon the amount of solution, it was necessary to know the variation in the capacity for different degrees of filling. Instead of making new determinations I employed the values obtained by Professor Kohlrausch for the same glass and the same degrees of filling.

Filling	460 cc.	470	480	490	500	510	520
Capacity	1.0685	1.0489	1.0314	1.0155	1.000	0.9855	0.9715

The value for 500 cc. (Hg. at 0°) was determined as given above.

Temperature and Temperature Coefficient.

With very little difficulty the observations were all made at 18°. The room in which I worked had the sun only for a short time in the morning.

If the solution in the bottle became too warm, it was cooled from the outside by means of a piece of ice, or by moistening the outside and thus cooling by evaporation. If the solution became too cool, it was warmed by the hand until the correct temperature was obtained. I am sure that the variation in the temperature was never greater than 0.02° from 18°, as the thermometer could be read to this degree of exactness. In two or three cases I began with a temperature of 18°, and after forty minutes there was no perceptible change.

To avoid parallax I used a vision line drawn on the window, its position being determined in the usual manner. The temperature coefficients were determined from the normal solutions.

Salts Investigated.

The following salts were investigated: Calcium sulphate, calcium chloride, calcium nitrate, calcium acetate, strontium chloride, strontium nitrate, strontium acetate, barium acetate, silver acetate, potassium oxalate.

The following methods were employed for making the individual solutions:—

$CaSO_4$: The water of crystallization was first driven off and then the required amount of salt weighed out. Owing to the insolubility of the salt, only solutions having strengths of $m=0.01$ and under were investigated. 0.3400 g. was weighed out and then diluted to $\frac{1}{2}$ liter.

$CaCl_2$: The salt was first heated for two hours above 200° in order to drive off the water of crystallization, then cooled in a dessicator. 27.713 g. were weighed out and diluted to $\frac{1}{2}$ liter.

$Ca(NO_3)_2$: Made according to specific gravity. Spec. Grav. of the original solution 1.1141. According to Kohlrausch this denotes 13.822 g. of salt in 100 g. of solution. Since a normal solution requires 82.04 g. salt in a liter, 593.02 g. of the solution were weighed out and diluted to a liter.

$Ca(C_2H_3O_2)_2$: Made according to specific gravity. Spec. Grav. of the original solution 1.1443. According to Hager this denotes 27.234 g. of salt in 100 g. of solution. Normal requires 79.01 g. of salt in a liter of solution. So 289.86 g. were weighed out and diluted to a liter.

$SrCl_2$: Made according to specific gravity. Spec. Grav. of original solution 1.1343. According to Kohlrausch this denotes 13.922 g. salt in 100 g. of solution. Normal requires 79.20 g. in a liter. So 568.38 g. were weighed out and diluted to a liter.

$Sr(NO_3)_2$: The salt was first recrystallized, dried at 75–80°, and then 105.79 g. were weighed out.

$Sr(C_2H_3O_2)_2$: The amount of water of crystallization was estimated and found to be 4.1 per cent, thus denoting the presence of $\frac{1}{2}$ molecule of water. Then 107.2595 g. were weighed out.

$Ba(C_2H_3O_2)_2$: Made according to specific gravity. Spec. Grav. of original solution 1.1724. According to Franz this denotes 22.349 g. of salt in 100 g. of solution. Normal solution requires 127.509 g. of salt in a liter of water. 570.03 g. of the solution were weighed out and diluted to a liter.

$K_2C_2O_4$: The salt was first well dried over H_2SO_4, and then 92.113 g. were weighed out. (Reckoning 1 mol. of water.)

$AgC_2H_3O_2$: The salt was weighed out directly. Owing to its

slight solubility, solutions from $m=0.01$ and under were the only ones investigated. (The salt is soluble 1 part in 98 of water.) An attempt was made to make a solution $m=0.05$, but after this had stood in a dark room for three days a precipitate began to form, and so the attempt was abandoned. All the investigations with this salt were made in a room illuminated by gaslight only. For the solution $m=0.01$, 0.8347 g. of the salt was weighed out and diluted to $\frac{1}{2}$ liter. The specific gravities of the normal solutions are given above.

The Water Used.

The water for the very dilute solutions was obtained by triple distillation, the last two distillations being made in a tinned copper boiler having a tin cooler. The boiler was heated by a large Bunsen flame, and the products of combustion were led off into the chimney. The required purity was attained in about an hour and a half after the water began to boil; then for about three hours water was obtained having a conductivity between $0.75 \cdot 10^{-10}$ and $1.5 \cdot 10^{-10}$. In a few cases the conductivity was only $0.68 \cdot 10^{-10}$, so that its average conductivity was about $1.00 \cdot 10^{-10}$.

The water was kept in glass stoppered bottles covered by a bell jar.

It has been noticed by others, as well as by myself, that after the water has stood for a few days the conductivity has decreased from what it was directly after distilling. For example, water distilled May 5 had a conductivity of $1.095 \cdot 10^{-10}$. On the 12th it was $1.019 \cdot 10^{-10}$, and on the 18th $0.997 \cdot 10^{-10}$.

Results.

Professor Kohlrausch having investigated the solutions of $CaCl_2$, $Ca(NO_3)_2$, and $SrCl_2$, for values of $m=1.00$ and above, I used only those having a less value. His work was based upon per cent of salt, and not upon the gram equivalent, and so his values for the normal solutions and their multiples are interpolated. In the case of $Ca(NO_3)_2$ a slight difference occurred, in that he found $K=541.0 \cdot 10^{-8}$ (K=molecular conductivity), while I found $536.4 \cdot 10^{-8}$.

The first columns in the following table contain the values for

m; the second the observed conductivity diminished by the conductivity of the water. All the observations were made at 18° unless otherwise indicated.

TABLE I.

$\frac{1}{2}CaSO_4$.		$\frac{1}{2}CaCl_2$.	
m	$k_{18} \cdot 10^{10}$.	m	$k_{18} \cdot 10^{10}$.
water	(1.465)	water	(1.603)
0.0001	10.789	0.0001018	10.983
0.0005	51.234	0.0002034	21.686
0.0010	97.714	0.0006079	64.084
0.0050	402.30	0.001009	105.17
0.0100	719.81	0.002016	208.69
0.0100	(815.42 $t = 23°.77$)	0.006024	594.35
		0.01	964.67
		0.05	4341.6
		0.10	8218.0
		0.50	35008.0
		1.0	63310.0
		2.0	108300.0
		3.0	138900.0
		4.0	158300.0
		5.0	166600.0
		6.0	164400.0
$AgC_2H_3O_2$.			
water	(1.206)		
0.0001053	8.395		
0.0002083	16.687		
0.0006000	48.108		
0.0009615	76.844		
0.0050	388.68		
0.0100	750.40		
$\frac{1}{2}Ca(NO_3)_2$.		$\frac{1}{2}Ca(C_2H_3O_2)_2$.	
water	(1.663)	water	(1.345)
0.0001018	11.138	0.0001018	7.387
0.0002034	22.058	0.0002034	14.417
0.0006079	64.499	0.0006079	42.154
0.001009	105.99	0.001009	69.084
0.002016	208.11	0.002016	135.44
0.006024	597.59	0.006024	383.61
0.01	963.3	0.01	616.34
0.05	4266.0	0.05	2596.9
0.10	7948.0	0.10	4663.6
0.50	31711.0	0.50	15972.0
1.0	53640.0	1.00	23708.0
2.0	81800.0	1.00	(28120.0 $t = 26°.00$)
3.0	94600.0		
4.0	98300.0	2.00	29752.0
5.0	94600.0	3.00	27108.0
6.0	84500.0		

TABLE I. (*continued*).

$\frac{1}{2}$ $SrCl_2$.		$\frac{1}{2}$ $Sr(NO_3)_2$.	
m	$k_{18} \cdot 10^{10}$.	m	$k_{18} \cdot 10^{10}$.
water	(1.024)	water	(1.095)
0.0001018	11.449	0.0001018	10.623
0.0002034	22.564	0.0002034	21.056
0.0006079	65.769	0.0006079	61.652
0.001009	107.90	0.001009	101.37
0.002016	212.05	0.002016	198.74
0.006024	608.34	0.006024	568.26
0.01	986.62	0.01	919.98
0.05	4404.7	0.05	4009.0
0.10	8492.0	0.10	7462.8
0.50	35396.0	0.50	28858.0
1.0	63890.0	1.0	47837.0
2.0	108200.0	1.0	(56820.0, $t = 26.°$)
3.0	138700.0		
3.5	149900.0	3.00	80530.0
$\frac{1}{2}$ $Sr(C_2H_3O_2)_2$.		$\frac{1}{2}$ $Ba(C_2H_3O_2)_2$.	
water	(1.222)	water	(1.019)
0.0001018	7.837	0.00009990	7.699
0.0002034	15.626	0.0001996	15.373
0.0006079	46.367	0.0005964	45.260
0.001009	76.356	0.0009901	74.266
0.002016	149.02	0.001978	145.84
0.006024	426.97	0.005911	415.84
0.01	687.53	0.009814	670.09
0.05	2936.6	0.05	2939.2
0.10	5328.7	0.10	5390.6
0.50	18920.0	0.50	19754.0
1.0	29126.0	1.0	(31169.0, $t = 26.°$)
2.0	36577.0	1.0	
3.0	34976.0	2.0	42203.

$\frac{1}{2}$ $K_2C_2O_4$.			
m	$k_{18} \cdot 10^{10}$.	m	$k_{18} \cdot 10^{10}$.
water	(0.997)	0.01	1054.67
0.0001018	11.926	0.05	4693.4
0.0002034	23.368	0.10	8839.1
0.0006079	69.648	0.50	37570.0
0.001009	114.75	1.0	68783.0
0.002016	226.57	1.5	95900.0
0.006024	650.73		

In Table II. the gram equivalents m and the molecular conductivity $\frac{k}{m}$ are given.

TABLE II.

$\frac{1}{2}CaSO_4$.		$\frac{1}{2}CaCl_2$.		$\frac{1}{2}Ca(NO_3)_2$.	$\frac{1}{2}Ca(C_2H_3O_2)_2$.
m	$\frac{k}{m} \cdot 10^3$.	m	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.
0.0001	1079.0	0.0001	1078.9	1094.1	725.6
0.0005	1025.0	0.0002	1066.2	1084.5	708.8
0.001	977.1	0.0006	1054.2	1061.0	693.4
0.005	804.6	0.001	1042.3	1050.5	684.7
0.01	719.8	0.002	1035.2	1032.3	671.8
		0.006	986.7	992.0	636.8
$AgC_2H_3O_2$.		0.01	964.7	963.3	616.3
		0.05	868.3	853.2	519.4
0.0001	797.2	0.1	821.8	794.8	466.4
0.0002	801.1	0.5	700.2	634.2	319.4
0.0006	801.8	1.0	633.0	536.4	237.1
0.001	799.2	2.0	541.0	409.0	148.8
0.005	777.4	3.0	463.0	315.0	90.4
0.01	750.4	4.0	396.0	246.0	
		5.0	333.0	189.0	
		6.0	274.0	141.0	

$\frac{1}{2}SrCl_2$.		$\frac{1}{2}Sr(NO_3)_2$.	$\frac{1}{2}Sr(C_2H_3O_2)_2$.	$\frac{1}{2}Ba(C_2H_3O_2)_2$.	$\frac{1}{2}K_2C_2O_4$.
m	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.	$\frac{k}{m} \cdot 10^3$.
0.0001	1124.7	1043.5	769.8	770.7	1171.5
0.0002	1109.4	1035.2	768.3	770.2	1148.9
0.0006	1081.9	1014.2	762.7	758.9	1145.7
0.001	1069.4	1004.7	756.8	750.1	1137.4
0.002	1051.8	985.8	737.4	737.3	1123.9
0.006	1009.9	943.3	708.8	703.5	1080.2
0.01	986.6	920.0	687.5	682.8	1054.7
0.05	880.9	801.8	587.3	587.8	938.7
0.1	849.2	746.3	532.9	539.1	883.9
0.5	707.9	577.2	378.4	395.1	751.4
1.0	639.0	478.0	291.2	311.7	688.0
1.5	588.0				639.0
2.0	541.0		182.8	211.0	
2.5	500.0				
3.0	462.0	268.4	116.6		
3.5	428.0				

Graphic Reproduction of the Molecular Conductivity.

In the curves shown in Fig. 1, the values for $\frac{k}{m}$ are used as ordinates and the values for $m^{\frac{1}{2}}$ as abscissæ. Thus we can represent the course of the curve for all possible degrees of concentrations in a comparatively small space. The curves are constructed directly from the results obtained, excepting in a few cases where they are made a little more regular than the observations give, although the change is very slight.

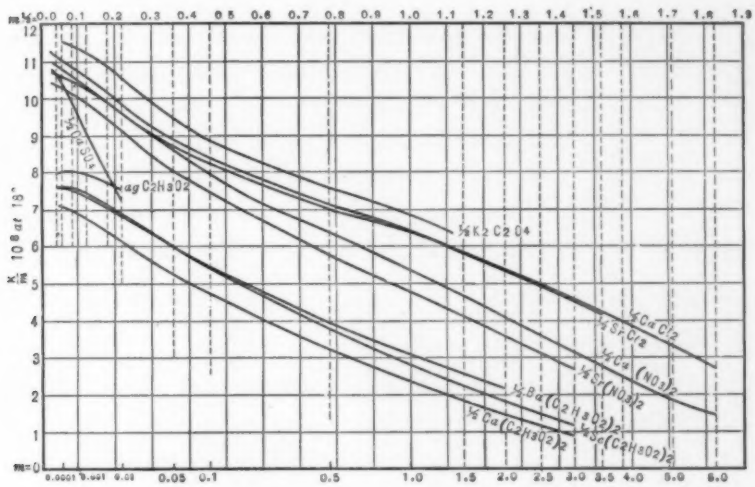

Fig. 1.

Temperature Coefficient.

The following tables contain the temperature coefficient for the normal solutions excepting for $CaSO_4$, where the value is for $m = 0.01$.

The values for $CaCl_2$, $Ca(NO_3)_2$, and $SrCl_2$ are those obtained by Professor Kohlrausch.

TABLE III.

Salt.	$\frac{\Delta k}{k_{18}}$	Salt.	$\frac{\Delta k}{k_{18}}$
$\frac{1}{2}$ $CaSO_4$	0.023	$\frac{1}{2}$ $SrCl_2$	0.0212
$\frac{1}{2}$ $CaCl_2$	0.0213	$\frac{1}{2}$ $Sr(NO_3)_2$	0.0224
$\frac{1}{2}$ $Ca(NO_3)_2$	0.0219	$\frac{1}{2}$ $Ba(C_2H_3O_2)_2$	0.022
$\frac{1}{2}$ $Ca(C_2H_3O_2)_2$	0.023	$\frac{1}{2}$ $K_2C_2O_4$	0.0209

General Remarks.

The curves giving the molecular conductivity are, for the most part, entirely regular, and even in the most dilute solutions there is no tendency in the curve to change from its upward course.

In the case of $AgC_2H_3O_2$ three separate determinations were made, and each time the curve changed from an upward to a downward course. Professor Kohlrausch assisted in one of the series at which the dilutions were carried to $m=0.00001$, and then we obtained the value $\frac{k}{m}=782\cdot 10^{-8}$. This change in direction is quite characteristic for free acids or bases, but why it should occur with $AgC_2H_3O_2$, never having been observed with any other salt, is something I am unable to explain.

The salt had almost no odor of acetic acid. Perhaps a more thorough study of the acetates will explain this peculiarity.

The curve for $CaSO_4$ agrees in form very nearly with the curves for $MgSO_4$, $ZnSO_4$, and $CuSO_4$, as given by Professor Kohlrausch.

COLGATE UNIVERSITY, PHYSICAL DEPARTMENT.

THE APPARENT FORCES BETWEEN FINE SOLID PARTICLES TOTALLY IMMERSED IN LIQUIDS. II.

By W. J. A. Bliss.

Part II. Theoretical.

§ 14. In Part I. the phenomena of flocculation have been shown to be capable of close reproduction between two pieces of glass, at least so far as the effect of KOH is concerned. The evidence in the case of NaCl is indirect, but still strong. As these two substances are typical of the two classes as to effect on flocculation, these experiments furnish a very conclusive argument in favor of a purely physical explanation of the phenomena in question, rather than the one usually opposed to it, that there is a chemical change, at least in the coating, of the flocculated particles. The following discussion of the manner in which such phenomena might result from molecular forces may be divided into five heads: —

(1) Previous state of the theory. Sections 15–17.

(2) Proof that the force which tends to hold two submerged particles apart may be considered to be proportional to the difference between the coefficients of molecular force between a unit volume of solid and a unit volume of liquid, on the one hand, and two unit volumes of liquid on the other. Sections 18 and 19.

(3) Expression of these coefficients in terms of the densities of the solid, liquid, and salt in solution, and the constants of attraction between unit masses of these substances. Sections 20–23.

(4) Rough determination of the relative magnitudes which it is necessary to assign to these last constants in order to explain the phenomena of flocculation. Sections 24–27.

(5) Suggestions as to further investigations along these lines. Section 28.

§ 15. Barus[1] has advanced as a possible factor in a physical explanation, that the bombardment of two particles by the molecules of salt in solution forces them together in a manner similar to Lesage's theory of gravitation. This explanation is supported by the close resemblance between the order of substances in producing flocculation and their order as to electrolytic conductivity,[2] which suggests that both might alike depend on the number of ions. It fails to explain, however, the action of alkalies, since it would be difficult to suppose that in this case the ions were more active between the particles and so produced a repulsion.

§ 16. More probable explanations are those based upon the molecular forces between solid-and-solid, liquid-and-liquid, solid-and-liquid. Barus[3] suggests that the size of a particle of precipitate depends on these forces, the first two aiding, the other opposing, its growth. There is then a critical size, which determines the coarseness of the precipitate. Barus and Schneider[4] suppose each particle surrounded by an adherent envelope of liquid. The thickness of this shell depends upon the intensity of the attraction between solid and liquid. If the shells are large or the number of particles great, the latter cannot gather together or settle in a mass to the bottom without parting from these adherent envelopes. The shells must then shrink before flocculation or settling can take place. Such shrinkage is brought about by a decrease in the attraction between solid and liquid, due to rise in temperature; by the drawing together of the liquid molecules in freezing; or by a portion of the shell leaving the particles to adhere to salt molecules when such are introduced. Any of these causes should aid flocculation, as they actually do. Bodländer, in the paper already mentioned, has a similar but vaguer explanation.

§ 17. The most complete theory the writer has found is that of

[1] Bull. 36, U. S. Geol. Surv.

[2] Barus, *loc. cit.*, and also Am. Jour. Sci., February, 1889. Also, Bodländer, Gött. Nach., 1893, pp. 267–276.

[3] Barus, *loc. cit.*, p. 127.

[4] Zeitschrift für Phys. Chemie, VIII. 3, 1891, p. 290.

Professor Milton Whitney.[1] As variously stated in treatises on surface tension, if AB is the surface of separation of a liquid and some other substance, a molecule at P, Fig. 4, has a different potential from a molecule at Q, the circles about these points denoting the distance from them to which the molecular forces are operative. If the substance to the left of AB is air, the potential of Q is less than that of P, and surface tension results. If, on the other hand, this second substance is a solid, Q may be either at a greater or at a less potential than P. Hence, —

Fig. 4.

"If two small grains of clay, suspended in water, come close together, they may be attracted to each other or not, according to the potential of the water particles on the surface of the clay. If the potential of the surface particle is less than that of the particle in the interior of the mass of liquid, there will be surface tension, and the two grains will come together and be held with some force, as their close contact will diminish the number of surface particles in the liquid. If, on the other hand, the potential of the particle on the surface of the liquid is greater than that of the particle in the interior of the mass, the water surface around the grains will tend to enlarge, as there will be greater attraction for the particles there than in the interior of the mass of liquid, and the grains of clay will not come together, and will even be held apart, as their close contact would diminish the number of surface particles in the liquid around them."

K. Fuchs[2] has stated this last point very clearly and more generally: —

(1) If the molecules of the liquid are attracted more strongly by those of the solid than they are by other molecules of the liquid,

[1] U. S. Weather Bureau Bull. 4, 1892, pp. 19–20. The author states that the theory was suggested by Lord Rayleigh's article in the Phil. Mag., November and December, 1890, and also acknowledges advice and suggestions from Dr. A. L. Kimball. Notes of these hints, as well as correspondence with other scientific men, have been lent to the present writer, who acknowledges his own indebtedness thereto.

[2] Exner's Rep., XXV., pp. 735–742.

or than the molecules of solid attract one another, the potential energy will be a minimum, when each particle of solid is surrounded by a shell of liquid of the thickness of the radius of molecular force. The two particles will then repel each other if brought closer together than within twice this distance.

(2) If either of the forces, solid-solid or liquid-liquid, is greater than the force solid-liquid, the potential energy will be least when the two particles are approached as closely as possible. They will then attract.

These theories, as well as the treatment about to be given, require that the particles influenced be not very great compared with what is usually called "the sphere of molecular force." The radius of the latter is, according to Quincke, 0.000005 cm. The diameters of the clay particles are, according to Whitney, between 0.0005 and 0.00001 cm., *i.e.* from 100 times to twice the radius of attraction. According to Barus and Brewer they are ultra-microscopic, and the former considers 0.000005 a fair value, *i.e.* the same as the radius in question. Noting the dependence of the theory on a size of particles not much exceeding these values, we will now seek to pass from the general conception of a diminution in Potential Energy by a change in the relative position of the particles to the actual forces by which such change is brought about. For simplicity we limit our attention to two particles.

§ 18. Let the particles be rigid, homogeneous spheres, and let us assume the liquid about them homogeneous, and of the same density within the range of molecular forces. We will consider the effect of the solid on a unit volume of liquid at P, whose sphere of molecular action impinges on both spheres. The unit volume must, of course, be taken extremely minute.

(Fig. 5.) Let ABC and $A'B'C'$ be the sections of the two solid particles by a plane through their centers and through P. Let the circles $EFE'F'$ and $LMNS$ be drawn on P as a center, and cutting ABC and $A'B'C'$. They enclose a section of a spherical shell, of which P is the center. Draw the arcs EF and $E'F'$ symmetrical with BC and $B'C'$ as regards P. Then the resultant of the attraction of the spherical shell upon a small unit volume of liquid at P is made up of the attractions of several

pairs of equal volumes symmetrically situated as regards P, as follows:—

(1) $F'S'L'G'$ and $EMND$, whose resultant is zero, for they are both composed of solid, and are directly opposed to one another.

(2) $D'N'LG$ and $E'M'SF$, whose resultant is also zero, since both are liquid.

(3) $GLME$ and $G'L'M'E'$. For every element of one of these there is one in the other precisely similarly situated as regards P, but the one element composed of solid, the other of liquid. Therefore, if B be the attraction of a unit volume of the given

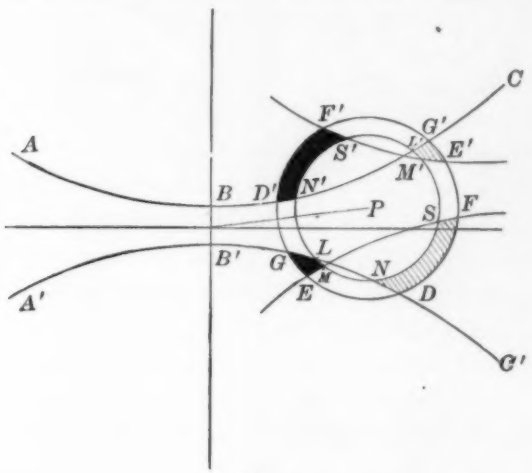

Fig. 5.

solid for one of the given liquid, at unit distance, and C the similar coefficient between unit volumes of liquid, the resultant of the two segments will be $(B-C)$ into an integral taken over either of the two, the force being taken positive when towards the solid.

(4) Similarly, the resultant of $D'N'S'F'$ and $DNSF$ will be $(B-C)$ into an integral taken over either of these segments.

Hence the resultant of the whole shell will be proportional to $(B-C)$. Taking the sum of all such shells which cut both solids, we get the total force upon the element P due to the presence of the two particles. Hence if a = radius of solid spheres; $e=BB'$, the distance between them; n = the distance of P from O, the

middle point of BB'; and ϕ the angle POB, then the force on unit volume at P is

$$p=(B-C)\,F(a, e, \phi, \text{and } r). \tag{1}$$

Considering the liquid between the spheres, each shell of liquid of radius r about O produces a pressure on all the liquid within it due to the force p, and hence on the two particles, tending to force them apart. Therefore resolving p along PO and integrating[1] throughout the liquid between them, we get the force Φ tending to separate the particles: —

$$\Phi=(B-C)\,F'(a, e). \tag{2}$$

The actual evaluation of F' without a knowledge of the law of variation of molecular attraction with the distance would, of course, be impossible. Even under the assumption that the law is that of the inverse fourth power, the writer has found it far from simple. The variation of the density, and probably the concentration of a salt solution near a solid surface, make it unlikely that B and C are accurately constant throughout the integration; but, while noting this assumption, we may take the above form as an approximation to the force introduced by the pressure of the liquid in trying to form a complete shell about each particle.

§ 19. The distance between the spheres is further affected by the attraction between the spheres themselves. Denoting by (ss) the coefficient of attraction between *unit masses* of the given solid, at unit distance, this force will be

$$\Psi=(ss)n^2F''(a, e), \tag{3}$$

where n is the density of the solid. Φ and Ψ, in the absence of electrical forces, may be assumed to be the only ones acting, and therefore the force *holding the particles together* is

$$R=(ss)n^2F''(a, e)-(B-C)F'(a, e). \tag{4}$$

§ 20. The coefficient $(B-C)$ is the only thing that changes in the value of this force when nothing is changed but the composi-

[1] This part of the process has since been found outlined by Barus and Schneider, Zeit. Phys. Chem. III. 3, 1891.

tion of the liquid. For a change in the latter, R increases as $(B-C)$ decreases. Since increased flocculation means an increase of the force holding the particles together, *i.e.* of R, increased flocculation means that $(B-C)$ has decreased. Hence, to explain the facts of flocculation, —

(1) $B-C$ must decrease when a trace of flocculent substance is added to pure water. Calling σ the mass of salt added to unit volume, —

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0}$$

must be negative for such substances.

(2) This quantity must be positive for alkalies such as KOH.

(3) Increase of concentration in the case of flocculent substances produces increased flocculation. In the case of alkalies it reverses the effect of a trace, and also causes strong flocculation. Therefore, $\frac{d^2(B-C)}{d\sigma^2}$ is negative for all substances.

The next step is then to find B and C in terms of σ.

§ 21. C is the measure of the attraction of two unit volumes of liquid. In a salt solution it is probably slightly greater near the solid than in a portion of the same solution further away,[1] and differs still more from the value at an air surface. It is therefore only roughly proportional to the surface tension as usually measured.

On the value of B there is no experimental evidence, so far as I am aware. It is, however, instructive to try the result of a simple hypothesis as to the form of both B and C. Let us start with pure water and denote by (ww) the mutual attraction of two unit *masses* of water. Thus for a density ρ of water we can write $C=\rho^2(www)$. So, if (sw) denote the attraction between a unit mass of the water and a unit mass of solid, and n is the density of the latter, $B=n\rho(sw)$.

$$\therefore B-C=\rho\{n(sw)-\rho(www)\}, \tag{5}$$

$$\frac{d(B-C)}{d\rho}=n(sw)-2\,\rho(www). \tag{6}$$

[1] J. J. Thomson's Applications of Dynamics to Phys. and Chem., p. 191.

Let us see from this equation what the effect of heating on flocculation teaches us as to the relative values of (ww) and (sw). Barus shows[1] that rise of temperature in pure water produces flocculation. Since ρ, the density of the water, decreases with heating, the condition that $B-C$ also decreases is that $n(sw)-2\rho(ww)$ shall be positive, *i.e.* $n(sw)>2\rho(ww)$. Since n for an individual clay particle is not far from 2.6, we have in round numbers, ρ being about 1

$$(sw)>\frac{(ww)}{1.3} \text{ or } \tfrac{3}{4}(ww). \tag{7}$$

Extending the above formulæ for B and C by the simple hypothesis that the effect of salt in very dilute solution is merely additive, we have for B in such a dilute solution,

$$B=\rho' n(sw)+\sigma n(st), \tag{8}$$

where (st) is the attraction of unit masses of salt and solid, and σ the mass of salt in unit volume. Similarly formed constants give for C,

$$C=\rho'^2(ww)+2\sigma\rho'(wt)+\sigma^2(tt), \tag{9}$$

where (tt) is the attraction between two unit masses of the salt, and (wt) between water and salt.

§ 22. A formula analogous to the above has since been found to be used by Volkmann[2] to express the surface tension of a mixture, densities being replaced by the volumes of the solutions mixed, and the constants (ww), etc., by their surface tensions independently. He mentions previous use of it by Poisson, and also quotes from O. E. Meyer[3] a similar expression for the viscosity of a mixture. Sutherland[4] finds a much more complicated expression to agree best with experimental results on surface tension and compressibility, the law of the inverse fourth power being assumed, and also a number of other conditions. As nearly as possible in the present notation his formula is

$$C=\bar{\rho}^2\cdot\frac{(1+n)(ww)(tt)}{(tt)+n(ww)}, \tag{10}$$

[1] Bull. 36 U. S. Geol. Surv., p. 23.
[2] Wied. Ann., Vol. XVI., p. 321, and Vol. XVII., p. 384.
[3] Pogg. Ann. 113, p. 405, 1861.
[4] Phil. Mag., March, 1893.

where $\bar{\rho}$ is the density of the liquid as a whole, and n the number of salt molecules to one of water. The complexity of this formula may very probably be due, at least in the case of surface tension, to the fact that while the densities and concentration of the solution are those in the interior, the value of C concerned is that for volumes near an air surface, where both the former quantities might be very much modified. The mathematical work, however, of connecting such a constant with experimental results is very complicated, and in the present state of science involves so many assumptions as to be inconclusive, and it seems, therefore, hardly advisable to abandon the simpler expression found in § 21 for the above, at least for the present purpose.

§ 23. The value of ρ', *i.e.* the weight of water in unit volume of the solution after the salt has been put into an amount σ per unit of volume, may be denoted closely enough for present purposes (very dilute solutions) by $\rho' = \rho - \alpha\sigma$, where α is a small constant calculated from densities of salt solutions. A few values[1] are given below:—

Flocculent substances,

NaCl and KCl, $\alpha = 0.3$; HCl, $\alpha = 0.4$.

Substances which prevent flocculation,

KOH, $\alpha = 0.07$; Borax, $\alpha = 0.8$; NH_4OH, $\alpha = 1.1$.

Introducing this value of ρ' in our values for B and C,

$$B = (\rho - \alpha\sigma)n(sw) + \sigma n\{(st) - \alpha(sw)\} = \rho n(sw) + \sigma n\{(st) - \alpha(sw)\}. \quad (11)$$

$$C = \rho^2(ww) + 2\rho\sigma\{(wt) - \alpha(ww)\} + \sigma^2\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (12)$$

$$B - C = \rho n(sw) - \rho^2(ww) + \sigma[n\{(st) - \alpha(sw)\} - 2\rho\{(wt) - \alpha(ww)\}] - \sigma^2\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (13)$$

§ 24. This equation connects B and C with the density of salt in the solution, and in order to find the effect of an addition of salt on the force holding the particles together, we differentiate with regard to σ:—

$$\frac{d(B-C)}{d\sigma} = n\{(st) - \alpha(sw)\} - 2\rho\{(wt) - \alpha(ww)\} - 2\sigma\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (14)$$

[1] Landholt and Börnstein's Tabellen; Röntgen & Schneider, Wied. Ann.

By now putting $\sigma=0$, we get the effect on flocculation of the first trace of salt: —

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0} = n(st) + 2\,\rho\alpha(wzw) - 2\,\rho(wt) - n\alpha(sw). \qquad (15)$$

But it was shown in § 21, that in order to account for flocculation by rise of temperature,

$$(sw) > \frac{2\,\rho}{n}(wzw).$$

$\therefore$ Assuming $\rho=1$, and n, for clay $=2.6$,

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0} = 2.6(st) - 2(wt) - \alpha \times \text{a positive quantity.} \qquad (16)$$

If the right hand member is negative, the first trace of salt causes flocculation; *i.e.* salts where $(st) < \frac{3}{4}(wt)$, or which attract the given clay only three-quarters as strongly as they do water, belong to the flocculent class. On the other hand, if (st) is considerably greater than (wt), $B-C$ will increase upon the addition of the first trace of salt, and the latter belongs to the class like KOH, which prevents flocculation when only a trace is present. The value of α here makes a great difference, and KOH and borax, with small values of this constant, need attract the solid very little more than three-quarters as much as they do water; while ammonia, which very much reduces the water in unit volume, must have a very much larger relative attraction for the solid, or it would cause flocculation instead of preventing it.

§ 25. In order to find the conditions under which continued additions of salt always tend to increase the tendency to flocculation, even where the first trace has the opposite effect, we must apply the condition (3) of § 20; *i.e.* $\frac{d^2(B-C)}{d\sigma^2}$ is always negative. Hence, differentiating again in (14),

$$\frac{d^2(B-C)}{d\sigma^2} = -2\{(tt) - 2\,\alpha(wt) + \alpha^2(wzw)\}, \qquad (17)$$

so that the quantity in brackets must be positive for all substances tried, *i.e.* $(tt) + \alpha^2(wzw) > 2\,\alpha(wt)$.

For KOH, where $\alpha=0.07$, α^2 may be neglected, and in order to

account for the production of flocculation by an excess of KOH we need only suppose that $(tt) > 0.14(wt)$; that is, a comparatively weak attraction of KOH for itself as compared with its attraction for water is sufficient.

For NH_4OH, on the other hand, $\alpha = 1.1$, and the condition becomes $(tt) + 1.2(ww) > 2.2(wt)$, which means that the inter-attraction of ammonia and water is weak compared to the attraction of each for itself.

Similarly for flocculating substances, whose effect on flocculation increases *a fortiori* with the quantity present, the same equation holds, and, for example, in the case of NaCl, where $\alpha = 0.3$, becomes

$$(tt) + 0.09(ww) > 0.6\ (wt)\ ;$$

i.e. the lowest assignable value for the attraction of unit masses of salt for one another, must be not far from $\frac{1}{2}$ of the attraction between common salt and water.

§ 26. The last paragraph showed how from experiments on flocculation, assuming the present theory, rough relative values may be deduced for the coefficients of attraction between various soluble substances and water. Similarly, from the section before we get relative values of the coefficients between salts and water on the one hand, and salts and solids on the other. The solid specially referred to in the instances given is such clay as gives the results obtained by most experimenters on flocculation. With different solids the effects in flocculation might be very different, since n, the density, as well as the constants (ss), (st), and (sw), in the above equations would vary. For instance, Brewer[1] experimented with Hartford clay, and himself remarks upon the almost exactly opposite results obtained by him from those of most other experimenters. He found that even so small a trace as 0.0008 gr. of KOH per cu. cm. aided precipitation; while, on the other hand, a very dilute mixture of nitric and hydrochloric acid (one part to several thousand of water) held the clay in suspension. In such clay the attraction between the clay and KOH would be less than its attraction for the acids instead of greater. On the other hand, the experiments of the first part of the present paper showed that

[1] Memoir, National Academy of Sciences, February, 1883.

glass has about the same relative values of the coefficients as the more usual clays.

The results of § 25 are entirely independent of the solid, and concern only water and the substance dissolved therein.

§ 38. The most useful outcome of the above discussion seems to be the means afforded of comparing the consequences of the theory given, as stated in the results of the last sections, with our general information concerning the various substances. To this end they are summarized below in round numbers, the forces being measured between unit masses at unit distance. From the clay referred to is to be expressly excluded such clay as the Hartford clay of Brewer, which seems to be exceptional; while, on the other hand, about the same properties may be set down to glass as are here ascribed to clay.

(1) The force between clay and water is greater than three-quarters the attraction of water for itself.

(2) The attraction of ammonia for clay must considerably exceed that of ammonia for water. KOH and the substances of which it is typical must have an attraction for clay *greater* than three-fourths that between the salt and water, while flocculating substances such as NaCl must have an attraction for clay *less* than three-fourths that for water.

(3) The attraction of NaCl for itself must be at least as great as three-quarters its attraction for water. The attraction of KOH for itself need only be from one-tenth to two-tenths its attraction for water. The attraction of ammonia for itself, and of water for itself, must be at least as great as their mutual attraction; or at least if the attraction of ammonia for itself is not as great as its attraction for water, the deficiency must be made up by a very strong attraction of water for itself (relatively to the two other coefficients).

The relative attraction of KOH and salt for water in (3) is interesting in view of the heat evolved when KOH is dissolved, and other parallels between the above and well-known properties of the various substances will readily occur to the reader.

§ 28. The subject of flocculation is one of sufficient practical interest in connection with its effect upon soil texture, as well as

its action in sedimentation, to repay a direct study. Data are at present given for the most part only incidentally in describing experiments upon the rate of settling of sediments and precipitates. Its importance in this latter phenomenon has even to a large extent been overlooked, and the effect of traces of salts, ascribed to changes in the viscosity of the liquid and a variety of other causes, many of which are undoubtedly active enough to prevent the rate of settling from being more than a rough guide to the state of flocculation. Direct experiments might be made with a microscope, or perhaps by the colors of light transmitted through the suspended particles, and for merely scientific purposes they should be made on other substances besides soils. The writer proposes at once to try to extend the experiments of Part I. of the present article to a much greater range of salts, and also, if possible, by a modification of the apparatus, to obtain curves connecting the thickness of the liquid film intervening between the glass surfaces with the concentration of the solution.

Quantitative values of the constants in the theory just given could hardly be hoped for from experiments on flocculation, nor could the law of force be determined from them. The writer believes, however, that a process similar to the one here given, applied as rigorously as possible to the calculation of surface tensions of salt solutions and mixtures, would repay the very considerable labor of developing it. He has himself made a beginning, assuming the law of the inverse fourth power, but endeavoring to calculate the density in the surface film instead of assuming a probable value for it.

Note.

Since the work given in the above pages was done, there has appeared in the *Philosophical Magazine*, March, 1894, an article by Dr. G. Gore, in which he attacks in a different manner the relative attractions of various solids and salts. His method has the very great advantage of yielding quantitative results, but of a kind not readily interpreted. The experiments measure the rise in temperature of pure water and of various salt solutions when certain solids in the form of powder are poured

into them. The heat given to the liquid comes from the combination of several changes of energy.

(1) Heat absorbed by the separation of the solid particles from one another.

(2) Heat liberated by the liquid wetting the particles, *i.e.* replacing air in their surface films. This is the energy Dr. Gore believes he has measured.

(3) Further change of energy as the powder packs together at the bottom of the vessel and the liquid is squeezed out.

The combined effect of (1) and (3) is the change in the potential energy of the solid due to the change in compactness between a dry and a wet powder, which it does not seem proper to neglect. We consequently find a marked difference between his results and the phenomena of flocculation. In the latter pure clay is held in a more separated condition in pure water than in any solutions except extremely dilute ones of certain alkalies. Since Dr. Gore's solutions are 10 per cent, the heat liberated by the wetting of clay by pure water should be greater than when it is wet by any of his solutions. We find, on the contrary, that in the case of both silica and alumina the heat given out in wetting by dropping them into pure water has a medium value exceeded in the case of a number of solutions with each of the two solids. We should not perhaps expect pure silica and alumina to give exactly the same results as clay, but in view of the fact that such strong solutions have been found to flocculate a wide range of materials when in suspension, the discrepancy seems more likely to lie in the cause given above.

MINOR CONTRIBUTIONS.

Surface Tension of Water at Temperatures below Zero Degree Centigrade.

By W. J. Humphreys and J. F. Mohler.

THE ratio of the change of the surface tension of water to the change of its temperature is well known for all values of the latter from 0° C. to 80° C., and the object of the investigation described in this paper was to determine the value of this ratio for temperatures below zero.

The method adopted was that of measuring, at various definite temperatures, the height of a column of water in a vertical capillary tube.

Owing to small unavoidable irregularities in the bore, and the difficulty of determining the exact area and shape of its cross section at the various positions occupied by the free surface of the water in the tube, should its position be allowed to vary, it was found best to keep this surface fixed, and to alter the length of the column by changing the level of the water in which the lower end of the tube was immersed.

The apparatus devised and the method of using it will be readily understood by referring to Fig. 1, in which *T* is a long capillary tube, vertical for some distance, then horizontal, and finally ending in an inverted U, the end of which dips into pure water in the vessel *E*. This vessel rests on a suitable support *G* (a strip of heavy plate glass, a meter in length and five centimeters broad, was used), which in turn rests on the fulcrum *F* and the vernier calipers *V*. The vertical portion *X* of the capillary tube is surrounded by a glass cylinder *K* about three centimeters in diameter and twenty centimeters long. During the investigation the top of the capillary tube was covered by a loosely fitting glass cap *S*, which protected the interior from dust. *R* served to keep *K* filled with cold brine of any desired temperature, the level of which was kept constant by the overflow pipe *O*. The microscope *M* was kept fixed in position, and furnished with a micrometer eyepiece, one of whose cross hairs was made to coincide with the image of the surface of the column of water in the capillary tube. The temperature was taken by two thermometers, the bulb of one being at the bottom of the cylinder *K*, and that of the other on a level with the microscope; but readings were not made when these differed by more than two-

tenths of a degree, and in all cases the temperature of the upper thermometer, which read to tenths, was that taken, as it marked the temperature of the surface of the water.

To insure a clean surface, the tube was well washed, before being drawn out into the capillary form, with strong nitric acid, water, alcohol, and ether, in the order named. The water used in the investigation had been redistilled in glass vessels from an alkaline solution of potassium permanganate, corks of all kinds being avoided; and the tube was always refilled just before taking a set of observations by drawing in the water through its top, thus obtaining a surface quite free from dirt of any kind. Previous to

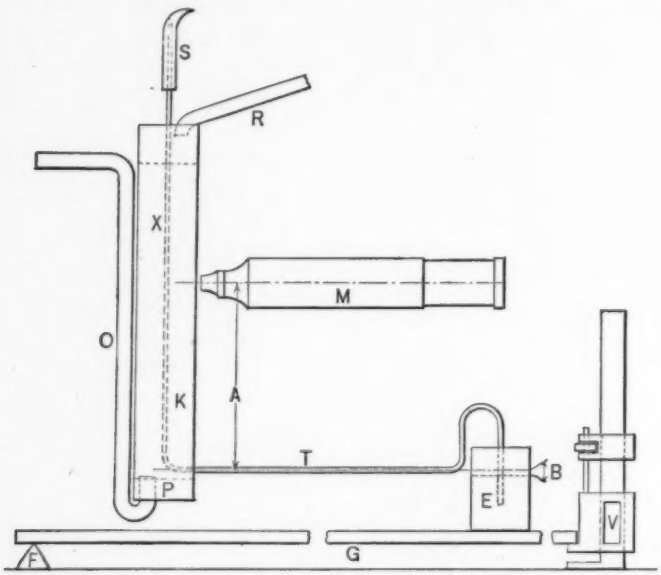

Fig. 1.

each filling the water was freed from absorbed air by being boiled under the receiver of an air pump. Before taking observations the portion *T* of the capillary tube was accurately leveled to avoid errors otherwise arising from the want of uniform density of the water in this part of the tube. The differences between this level and those of the top of the column in *X* and the surface of the water in *E* were measured by a cathetometer. The first of these differences of level gives the length *A* of the tables, and was kept constant during each set of readings; the second was varied by the vernier calipers *V*, so as to keep the top of the column at a definite position in *X*, determined by the cross hairs of the fixed microscope *M*. Before each reading the top of the column in *X* was temporarily raised to

insure complete wetting of the tube. It was found that slight tappings of the apparatus often caused the column to more readily take up its final position of rest. This precaution was taken while making the sets of readings marked III. and IV. It was likewise found that small drops of water would occasionally collect in the upper part of the tube X. This led to three sets of observations being discarded on account of complications thus introduced.

Referring now to the tables: T is the temperature of the column of water in X; A is the height of this column; B is the difference in level of the water in E and the horizontal portion T of the capillary tube, and is positive or negative according as the former is below or above the latter; C is A multiplied by the density of water at the corresponding temperatures, as given by Despretz; D is B multiplied by the density of water at the temperature of E — about 16°; h is $C + D$.

I.

T	A	B	C	D	h
+3.0	10.735	0.00	10.735	+0.0	10.735
+1.1	10.735	+0.024	10.734	+0.024	10.758
−0.9	10.735	+0.051	10.733	+0.051	10.786
−2.0	10.735	+0.088	10.732	+0.088	10.820
−3.0	10.735	+0.111	10.731	+0.111	10.842
−5.0	10.735	+0.156	10.728	+0.156	10.884

II.

T	A	B	C	D	h
+6.9	10.92	−0.341	10.920	−0.341	10.579
+4.7	10.92	−0.287	10.920	−0.287	10.643
+1.3	10.92	−0.216	10.920	−0.216	10.704
−0.9	10.92	−0.195	10.918	−0.195	10.723
−2.0	10.92	−0.160	10.917	−0.160	10.757
−4.2	10.92	−0.100	10.914	−0.100	10.814
−6.0	10.92	−0.040	10.910	−0.040	10.870
−7.2	10.92	+0.003	10.908	+0.003	10.911
−8.0	10.92	+0.027	10.905	+0.027	10.934

III.

T	*A*	*B*	*C*	*D*	*h*
+18.5	10.945	−0.508	10.929	−0.508	10.421
+ 5.35	10.945	−0.269	10.945	−0.269	10.676
+ 4.6	10.945	−0.251	10.945	−0.251	10.694
+ 3.5	10.945	−0.235	10.945	−0.235	10.710
+ 3.2	10.945	−0.228	10.945	−0.228	10.717
+ 2.5	10.945	−0.209	10.945	−0.209	10.736
+ 2.0	10.945	−0.201	10.945	−0.201	10.744
+ 1.4	10.945	−0.181	10.944	−0.181	10.763
+ 1.0	10.945	−0.172	10.944	−0.172	10.772
+ 0.1	10.945	−0.148	10.944	−0.148	10.796
− 0.4	10.945	−0.137	10.944	−0.137	10.807
− 2.2	10.945	−0.111	10.942	−0.111	10.831
− 2.8	10.945	−0.095	10.941	−0.095	10.846
− 3.5	10.945	−0.079	10.940	−0.079	10.861
− 4.2	10.945	−0.057	10.939	−0.057	10.882
− 6.0	10.945	−0.009	10.936	−0.009	10.927
− 7.5	10.945	+0.031	10.933	+0.031	10.964
− 8.2	10.945	+0.060	10.931	+0.060	10.991

While taking this set of observations, the upper part of the capillary tube was entirely free from small drops of water, and the column brought to rest by slightly tapping the apparatus before taking each reading.

IV.

T	*A*	*B*	*C*	*D*	*h*
−1.8	10.95	−0.119	10.947	−0.119	10.828
−2.75	10.95	−0.079	10.946	−0.079	10.867
−3.6	10.95	−0.056	10.945	−0.056	10.889
−4.2	10.95	−0.036	10.944	−0.036	10.908
−5.2	10.95	−0.029	10.943	−0.029	10.914
−6.7	10.95	+0.013	10.940	+0.013	10.953
−7.6	10.95	+0.052	10.938	+0.052	10.990
−8.3	10.95	+0.083	10.936	+0.083	11.019

The curves in Fig. 2, plotted from these tables, show the relation of temperature to h, the ordinates being h multiplied by ten, and the abscissæ the corresponding temperatures. These curves very nearly coincide with

the straight line $h_t = h_0(1-.002014t)$, where h_t is h at the temperature t; and, as the surface tension is proportional to h, this gives, for the value of the surface tension of water at temperature $t°$ C., $T_t = T_0(1-.002014\,t)$, where T_0 is the value of the surface tension at zero degrees Centigrade.

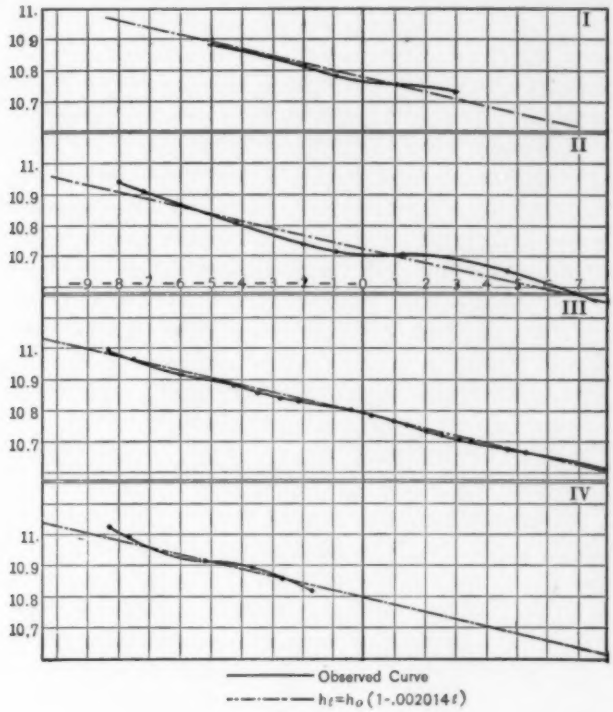

Fig. 2.

Therefore, according to the above observations, the ratio of the change of surface tension of water to the change of temperature is continuous and approximately equal to $.002014T_0$ throughout the range of temperature observed, *i.e.* $-8°.3$ C. to $+18°.5$ C.

This result is in close agreement with those obtained by many observers for temperatures above zero. Thus

Volkman gives $T_t = T_0(1-.001829t)$,[1]
Tinberg gives $T_t = T_0(1-.002208t)$,[2]
Jäger gives $T_t = T_0(1-.00232t)$.[3]

[1] Wied. Ann., 17, p. 353, 1882.
[2] Wied. Ann., 30, p. 545, 1887.
[3] Sitz. Wien. Akad., 100, p. 258, 1891.

JOHNS HOPKINS UNIVERSITY, January, 1895.

VARIATION OF INTERNAL RESISTANCE OF A VOLTAIC CELL WITH CURRENT.

BY HENRY S. CARHART.

IT has long been known that the internal resistance of a voltaic cell, when at a constant temperature, has not a fixed and finite value, but that it is a function of the current flowing through it. The methods commonly employed to measure this resistance are not sufficiently exact to exhibit the relationship in question with satisfactory accuracy. But if the condenser method be employed,[1] together with certain auxiliary appliances to secure very brief and uniform closing of the circuit through different external resistances, while the potential difference between the battery terminals is measured within this short interval, then results can be obtained which plot as a smooth curve.

The resistance measured is a quantity satisfying the equation

$$r = R\frac{E - E'}{E'}, \text{ or } \frac{E}{R + r} = \frac{E'}{R} = I,$$

where r is the internal resistance, E the electromotive force of the cell, and E' the potential difference between the terminals when closed through an external resistance R. To determine the relation between r and I, the potential difference E' must be measured with different external resistances in succession. For this purpose, the operations of closing the circuit, charging the condenser, discharging through a ballistic galvanometer, and finally opening the circuit, must be done by some mechanical device, by which all of them can be repeated in precisely the same interval of time. The disturbing influences due to absorption of the condenser and polarization of the cell are then as nearly eliminated as possible.

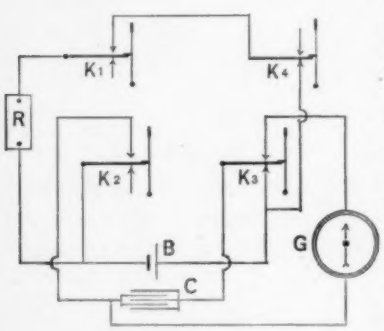

Fig. 1.

For this purpose I have made use of a pendulum consisting of a long narrow frame pivoted at the top, and carrying a heavy bob at the bottom. The bob swings between two curved rails, concentric with the axis of sus-

[1] Carhart's Primary Batteries, p. 116.

pension of the pendulum, and each rail supports two keys, which can be clamped on it in any desired position. A vertical lever on each key holds it closed on the lower contact; but when the pendulum sweeps over the rails it throws these levers over, and allows the spring keys to make contact on the upper point. The contacts are all platinum, and the base and pillars of the keys are hard rubber. When care is taken to adjust the contacts properly and to keep them free from dust, their performance is in every way satisfactory.

Figure 1 shows the connections for the measurements in hand. Keys K_1 and K_4 are on one rail, while K_2 and K_3 are on the other. When the lever of K_1 is thrown forward while that of K_4 is up, the battery circuit is closed through the resistance R. When the lever of K_2 is thrown over while that of K_3 is up, the battery is charging the condenser C; but as soon as the lever K_3 is thrown over, the cell is disconnected from the condenser, and the latter is instantly discharged through the galvanometer G. The pendulum swings from left to right on removing a detent. If all the levers are up, it closes the battery circuit on reaching K_1, charges the condenser by throwing over lever K_2, discharges it through the galvanometer by means of K_3, and finally opens the battery circuit on passing K_4. The key levers remain forward out of the way of the pendulum bar as it swings back again to the detent. The keys can be set as close together as desired. The length of the pendulum is such that its period is a second. Hence the time during which the battery circuit remains closed can be calculated. To get the deflection proportional to the total electromotive of the cell, the levers of K_1 and K_4 are both left down. The pendulum then charges and discharges the condenser, the circuit through R remaining open.

The change of resistance with the current is exhibited in a marked degree by "dry cells." The table contains the data of a series of measurements

d_1	d_2	R	r	I
271	258	400	21.1	0.0028
	249	200	17.7	0.0056
	238	100	13.9	0.0106
	227	50	9.7	0.0203
271	223	40	8.6	0.0249
	218	30	7.3	0.0324
	212	20	5.56	0.0473
	204	15	4.93	0.0607
	194	10	3.96	0.0868
271	172	5	2.87	0.1538
	164	4	2.59	0.1838
270	153	3	2.29	0.2289

on a Gassner cell, whose electromotive force was 1.213 volts. The first column contains the deflections due to charging the condenser with the whole electromotive force of the cell, and it will be seen that the polarization was inappreciable. The second column contains the deflections due to charging the condenser with the potential difference at the extremities of the cell when closed through the resistances in the third column. The fourth column contains the resulting internal resistances, and the last column the currents.

In Fig. 2 these internal resistances and the corresponding currents are plotted as coördinates. It cannot be objected that the relatively low

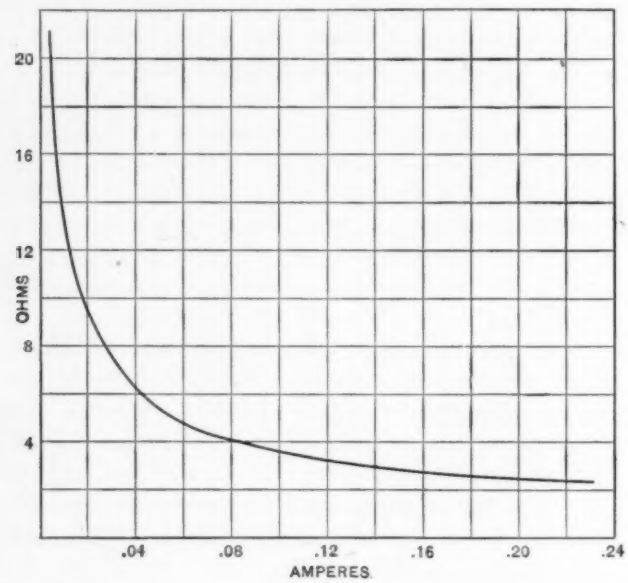

Fig. 2.

resistances with the larger currents are due to polarization; for, while it was demonstrated that polarization did occur within the small time interval required for the pendulum to swing from K_1 to K_4, yet the effect of such polarization is to diminish the potential difference between the terminals of the cell when on closed circuit, and this effect increases the computed internal resistance.

The Gessner cell was an old one, and its internal resistance was above the average; but other dry cells show the same characteristic curve, differing only in the relative values of r.

A Daniell cell shows a similar decrease in r with increase in current, but the decrease is much smaller, and the curve is more nearly a straight line.

UNIVERSITY OF MICHIGAN, January, 1895.

NEW BOOKS.

Manual of Physico-Chemical Measurements. By WILHELM OSTWALD, translated by JAMES WALKER. pp. xii + 255. New York and London, Macmillan & Co., 1894.

The above translation of Professor Ostwald's latest contribution to physical chemistry fills a much felt want in our literature. It is not, as might be inferred from its title, intended as a laboratory guide for the beginner, but rather, as the author states in his preface, for the more advanced student already familiar with physical and chemical manipulation who desires to become acquainted with the various methods now employed in physico-chemical investigations. To the investigator, too, the little work will prove of interest and value, abounding as it does in practical hints and suggestions, the result of the author's own extensive experience. The value of the work is also materially increased by numerous references to original memoirs.

Having in view this more mature class of readers, the author has presented his subject not on the usual plan of a laboratory manual, with descriptions for the performance of set experiments, but rather as a general, and often critical, discussion under separate chapters of the various classes of measurements usually met with in practice. The first chapter on calculation is devoted to an elementary discussion of observations, particular stress being laid on the importance of observing rules for the retention of significant figures. It is only to be regretted that the importance of the graphical method is not brought into more prominence in this connection.

Six chapters follow of an introductory character, four of which are devoted to the usual methods of measuring length, mass, pressure, and temperature. Of the other two, one is devoted to a description and valuable criticism of a number of thermostats, most of which have been tried in the author's laboratory. The other chapter is devoted to glass blowing. Here, as indeed throughout the book, we find emphasized the author's conviction of the importance to the investigator of being able to construct his more simple apparatus. This is of particular importance to the physical chemist, as the necessary equipment for investigations in this branch of science is usually much less elaborate and costly than that required for purely physical researches.

A description of physico-chemical methods proper begins with a discussion of specific gravity determinations in Chapter VIII. Of the methods in general use the author gives preference to the Sprengel-Ostwald form of pyknometer for liquids, and the method of "floating" when applicable for solids. Particularly noteworthy in the following chapter, on methods for determining the physical properties of liquids, are the methods worked out in the author's laboratory for determining the critical constants. The method for critical pressure consists simply in unequally heating the capillary containing the substance under investigation, so that the upper part is above, the lower part below the critical temperature, and observing the pressure at which the meniscus disappears.

Following this are chapters on calorimetric and optical measurements, the latter including calorimetric and spectrophotometric methods, and the essential processes of photography. A special chapter is devoted to solubility determinations, as work along this line has proved, and doubtless will continue to prove, of the greatest value in solving problems connected with the theory of solutions. The well-known boiling and freezing point methods of Beckmann for determining the molecular weight of substances in solution, find, of course, their place in the work.

The chapter on electrical measurements is devoted almost wholly to measurements of the electromotive force of voltaic cells, and of the conductivity of electrolytes. In connection with the former will be found many new and valuable suggestions to persons working in this field. First are described the form and construction of various standards of electromotive force, viz., the Clark, Gouy, and v. Helmholtz cells. Following are several special methods, mostly based on Poggendorff's method, for measuring electromotive force, in all of which a Lippmann's electrometer is strongly recommended as indicating instrument. Particular attention is given to the measurement of very small potential differences, and three forms of Lippmann's electrometer, varying in sensitiveness from 0.001 to 0.0001 volt or even less, are described. My own experience confirms completely all the author claims for these very simple and useful instruments.

Another suggestion which it is to be hoped may meet with general acceptance is the adoption as normal electrode against which to measure the absolute potential difference between metals and liquids, of mercury covered with a layer of calomel in a normal solution of potassium chloride. The potential difference between the mercury and the solution is, according to our most accurate measurements, 0.540 volt. This electrode is easily constructed, its potential is very constant, and it possesses the additional advantage of reducing the contact potential at the liquid junction to a minimum, the velocity of migration of chlorine and potassium ions being very nearly equal.

Conductivity measurements are made by the well-known method of Kohlrausch. Convenient tables for calculating dissociation constants are given, and the electrical method of determining the basicity of acids explained. The last chapter is devoted to chemical dynamics, the rate of inversion of cane sugar, and the catalysis of methyl acetate being taken as illustrative examples.

In conclusion a word should be added in regard to the excellence of the translation and general appearance of the book, which is uniform with Dr. Walker's well-known translation of Ostwald's Grundriss der Allgemeinen Chemie.

H. M. GOODWIN.

The Work of Hertz and Some of his Successors. By OLIVER LODGE, F.R.S. 8vo, pp. 58. London, The Electrician Printing and Publishing Co., 1894.

This work is a reprint, with revision, from the *London Electrician*, and contains the substance of a lecture delivered at the Royal Institution. It is a semi-popular lecture rather than a critical review of the work which has been done along the line of Hertz' discoveries. Of the fifty-eight pages in the book about twenty, including most of the appendices, are devoted to the discussion of the effect of ultra-violet light on electric discharge. Though this is not Hertz' most important discovery, yet it is one possessing much interest, and the review on the subject, though brief, is very helpful. Fifteen pages are devoted to a description of the construction and use of an appliance which the author calls a "coherer." This is of especial interest because it furnishes a simple and effective method for detecting electric oscillations. In the remaining twenty-three pages is given a review of the general subject of electric waves.

The book does not by any means attempt to do for this subject what the very valuable review published by Lodge on Contact Electricity did for that.[1] In fact, the book is disappointing to one who might have hoped for a similar review on electric waves, and the more so, because with the exception of the part on the effect of ultra-violet light, it is quite deficient in references to original sources. Such an article would certainly be of the highest value; for, on account of the wealth of literature on the subject, it is difficult for a person not thoroughly posted to get a fair idea of the work which has been done along this line, of the relative importance of different methods, and of the results obtained. This criticism, however, is upon the title, which may be somewhat misleading, rather than upon the substance of the book.

[1] Phil. Mag. (5), Vol. 19.

As has been intimated, a most valuable part of the review is the description of an appliance which the author has made useful, and which he calls the "coherer." The "coherer" consists essentially of a poor contact, whose resistance is much diminished when it is subjected to electric oscillations. The easiest thing to use for this purpose is a tube of iron filings.[1] Lodge found that in the case of a tube which he used, the resistance decreased from 2500 ohms to 2100 ohms when the smallest kind of an electric discharge took place in its neighborhood. He explains this somewhat as follows : when two pieces of metal are in poor contact, only a very few of the molecules of one touch those of the other, and therefore the resistance is high ; but when the molecules of the two have been once well shaken together by the electric oscillations, they continue to cohere, and the resistance is very greatly decreased. When there are a number of such contacts, as in the case of a tube of iron filings, the effect is proportional to the intensity of the oscillations. Furthermore it was found that a mechanical jar would restore the tube to its original condition as far as resistance was concerned.

If such a tube be connected with a battery and a galvanometer, a change in the resistance can easily be shown. It was found that short oscillations affected the "coherer" more than longer ones, even though the longer ones were of much greater intensity. The author states that he was easily able to detect an exciting spark of high frequency at a distance of forty or sixty yards. In fact, it proved to be more easy to detect electric oscillations than to screen the "coherer" from their effect. But when this was properly done, so that only those waves coming from a given direction affected the "coherer," the reflection of electric radiation from metallic surfaces could be easily shown, also refraction through a paraffin prism, and even the focussing of electric waves by an ordinary nine-inch glass lens. Polarization effects were very easily secured, and in one case a diffraction effect was detected, although diffraction bands could not be shown.

The author hopes to use the "coherer" for quantitative work, but it seems doubtful whether it can be made as useful for this purpose as some other methods. As a simple means for showing qualitative effects, however, it is unsurpassed.

The book will certainly well repay perusal by any one interested in the Hertz phenomena.

C. D. CHILD.

[1] E. Brunly, C.R. Vol. 111., p. 785, and 112, p. 90.

An Elementary Treatise on Theoretical Mechanics. By A. ZIWET. Part III, Kinetics. 8vo, pp. viii+236. New York, Macmillan & Co., 1894.

The first two parts of Ziwet's *Mechanics* have already been noticed in the PHYSICAL REVIEW.[1] The third part, completing the work, is now before us.

The book is divided into three chapters, which treat respectively of the kinetics of a particle, of a rigid body, and of a variable system.

The first chapter opens with an elementary account of impulses and impact. Then are discussed the general equations of motion of a particle, the principle of energy, and the principle of areas. Extended applications of these principles to particles free to move and to particles under constraint are next given. The chapter closes with a short account of the Lagrange form of the equations of motion of a free particle.

In the chapter on the motion of a rigid body is given an elaborate account of the theory of moments of inertia — much of which belongs rather to the integral calculus. Next follows a very satisfactory treatment of the motion of a rigid body under continuous forces and of the initial motion due to impulses.

In the concluding chapter is considered the motion of a variable system subject to any conditions whatever. This chapter, though short, is very interesting from the use made of the Lagrange equations of motion.

Throughout the book the language is clear, the explanations concise, but sufficient for the student who has had a first-rate mathematical training. In the earlier portions examples with answers are given; in the later and more difficult parts there are references to books, mostly foreign, where examples may be found. It would seem as if the space taken up in referring to the same books, again and again, might, with more advantage to the student, have been devoted to some well-chosen examples.

In Art. 242 is a novelty which is hardly likely to find much favor. It is the substitution of the term *radius of inertia* for the old *radius of gyration*. The book is happily free from innovations of this kind.

The complete work is as a whole admirable for its systematic arrangement, and for its clear treatment of the more important principles of theoretical mechanics, and will be welcomed by students of the higher mathematics in our universities.

T. W. WRIGHT.

[1] Vol. I., No. 5.

Photographische Optik ohne mathematische Entwickelungen für Fachleute und Liebhaber. By Dr. ADOLF MIETHE. Large 8vo, pp. viii+153. Berlin, R. Mückenberger, 1893.

As indicated by the title, this little book is intended for those professional and amateur photographers who desire to obtain a knowledge of photographic optics without the use of mathematics. The author (well known to the photographic world as one of the originators of telephotographic objectives) "assumes nothing, neither physical nor mathematical attainments or conceptions. The sole aim of the work is universal intelligibility on the basis of common sense, clearness, simplicity."

The topics discussed are, in order, fundamental truths of optics, aberrations, diaphragms, the usual types, and the testing of photographic objectives. Of necessity, the treatment is not at all exhaustive, yet the language is, in general, so lucid as to give as good an idea of the subject as is possible, perhaps, without having recourse to mathematics. This clearness is much increased by the neat typography and illustrations; in particular, the two plates are of material assistance in the study of aberrations, including astigmatism.

The book may be heartily recommended to those who do not feel inclined to plunge into the mathematical intricacies of the subject; indeed, it deserves translation into English.

HENRY C. LOMB.

Proceedings of the International Electrical Congress, held in Chicago in 1893. New York, The American Institute of Electrical Engineers, 1894.

In this volume the Proceedings of the Congress are given in full, including the various papers presented, together with the discussion, and the official reports of the Chamber of Delegates. A report of this Congress, together with the list of papers presented and the principal business transacted by the Chamber of Delegates, is given in the PHYSICAL REVIEW, Vol. I., No. 3.

The American Annual of Photography and Photographic Almanac for 1895. pp. 438. New York, Scovill & Adams Co. (*Received.*)

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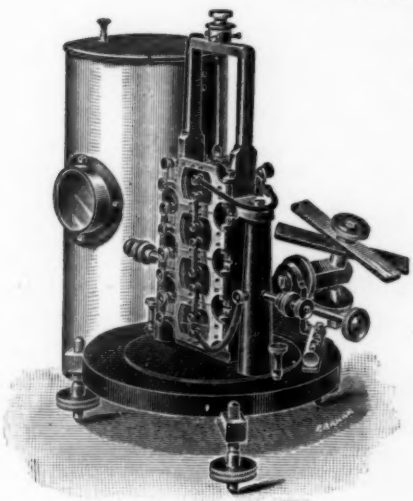

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